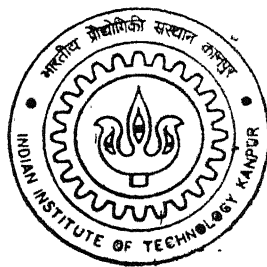


Surface Passivation of GaAs

By

Pawan Tyagi

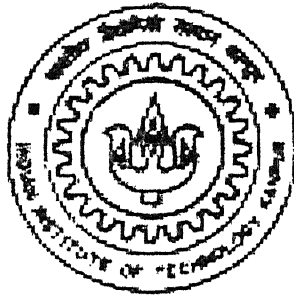
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DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING
Indian Institute of Technology Kanpur

Surface Passivation of GaAs

A Thesis Submitted
In partial fulfillment of the requirements
for the Degree of Master of Technology



By
Pawan Tyagi

to the

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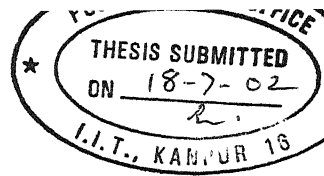
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Dedicated to
To my wife Punam
&
Parents



CERTIFICATE

This is to certify that the work accomplished in the thesis entitled "Surface Passivation of GaAs", by Pawan Tyagi, has been carried out under our supervision. We also state that this work has not been submitted anywhere for obtaining any other degree.

Dr R. Balasubramaniam
Department of Materials
and Metallurgical Engineering
I.I.T. Kanpur

Dr. Deepak Gupta
Department of Materials
and Metallurgical Engineering
I.I.T. Kanpur

Date: 17 July 02

Date:

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I.I.T. KANPUR

Abstract

Gallium Arsenide (GaAs) semiconductor has become one of the most favorite electronic materials for the development of advance devices. The use of GaAs is limited by the unsaturated surface states present at the interface of metal/GaAs and oxide/ GaAs interfaces. Effective passivation of GaAs surface is the key to overcome this problem. In present project new surface passivation methodologies have been attempted. Photoluminescence study of passivated GaAs surface affirms that the application of new surface passivation schemes ameliorated the GaAs surface electrical properties. This thesis report comprises of extensive literature survey on GaAs surface passivation followed by the details of novel surface passivation methodologies. A plausible mechanism behind the newly applied passivation methods is also presented.

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Chapter 1

Introduction

GaAs has direct band gap, high charge carrier mobility and high saturation drift velocity. These properties of GaAs make it superior over existing silicon (Si) semiconductor. High electron mobility in GaAs is very desirable for producing high frequency devices. Flexibility of manufacturing semi-insulating (SI) GaAs substrate is an added advantage, giving very low parasitic effect and allowing the fabrication of true monolithic circuit operating at high speed (beyond 1GHz) like MMIC (Monolithic microwave integrated circuit) device [1]. Besides this GaAs has high solid solubility for few elements like aluminium (Al), Indium (In) etc, which allows the maneuvering of energy band gap, facilitating the manufacturing of quantum devices [2]. Due to above mentioned merits, GaAs has become one of the most desirable electronic material for the fabrication of laser, hetero-junction bipolar transistors (HBT) and metal insulator field effect devices for the development of high speed optical and mobile communication system [3,4]. According to the latest report market of GaAs power transistor exists in following area Table1.

Table1. Market of GaAs power transistor in various field worldwide [5].

Application	Value (\$ million)	Share (%)
Cellular	93	38
Radar	12	5
Military	5	2
Avionics	7	3
Satellite	44	18
Others	83	34
Total	246	100

Source: Allied business intelligence's, Inc., 2000

In spite of possessing many superior electrical properties, GaAs has not been able to replace the utilization of Si from the fabrication of integrated circuit due to very high surface state density [6]. Surface state density present at the interface of Si and its oxide

is of the order of 10^{10} eV/cm², which does affect the charge carrier life time and the surface recombination velocity (SRV) greatly and this allows the fabrication of integrated on Si. Whereas, oxidized GaAs surface possess very high surface state density, of the order of 10^{13} eV/cm², which pin the Fermi level near the mid-gap [7-9]. Presence of high density of surface states increases the surface recombination velocity to 10^6 - 10^7 cm/seconds [10]. Consequently charge is depleted near the surface and cause the band bending. Poor electrical properties of oxidized GaAs preclude the use of GaAs for the manufacturing of advanced devices [11-13]. A brief description of problem associated with GaAs surface is presented in following section.

Termination of the surface states with the help of suitable passivant is the most apposite solution to this problem, while the realization of air stable passivated GaAs surface is yet to be achieved. Several passivation schemes were employed to overcome this problem of poor electrical properties of GaAs surface using many organic and inorganic elements and compounds. The description of the treatments methodologies will be presented in this thesis.

This thesis addresses the surface passivation of the GaAs, utilizing novel surface passivation schemes by using sulfur (S) and Fluorine (F) passivant in different combination. Additionally, the effect of electrochemical S passivation has also been studied.

Chapter 2

Literature Survey

This chapter initially introduces the problem associated with the GaAs surface. The numerous surface passivation techniques used thus far have been discussed. The information outlined will be used for understanding the results obtained in the project work.

2.1 Problem with GaAs surface:

It is well known that the oxidized GaAs surface, starting point for most of devices, has high surface state density due to the missing cation and anion from the surface [14]. It has been observed that ultra high vacuum (UHV) cleaved (110) GaAs surface has no surface state induced levels within the band gap, however UHV cleaved (100) surface exhibited nominal surface states density [15,16]. This observation provided sufficient support for the concept that the very high surface states density was due to the interaction of foreign elements with GaAs surface. There exist several models which define the origin of surface state on the GaAs surface. According to one group of researchers, oxidized GaAs produced the surface state in entire band gap [17]. However, it has also been suggested that the high density of mid gap surface states, which are mainly responsible for poor electrical properties of GaAs surface, are due to the presence of antisite defects [18,19].

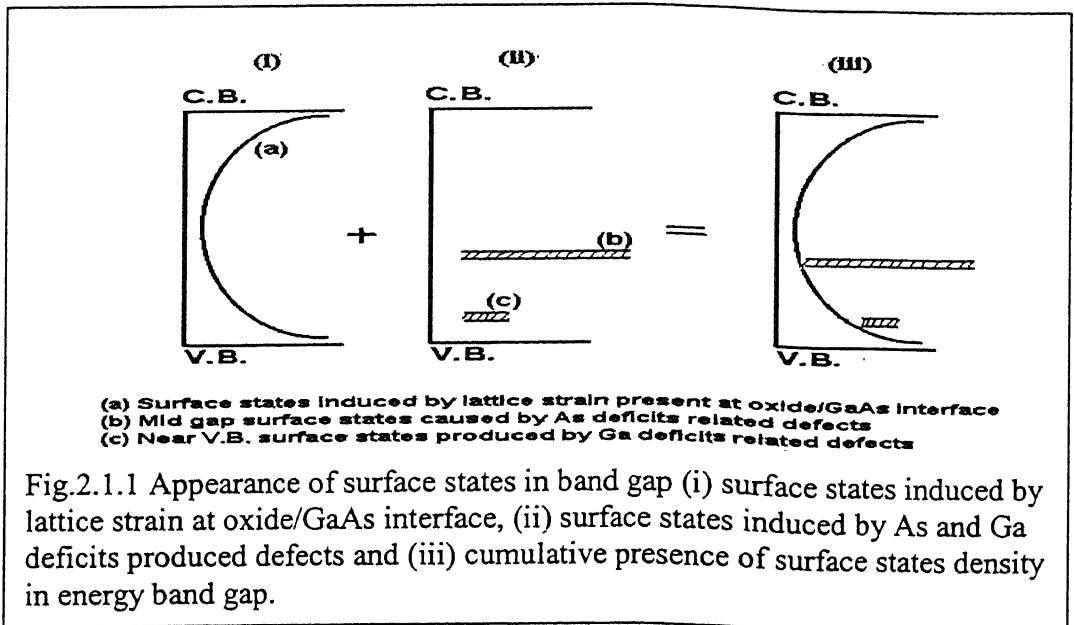
Spicer et al. [14] proposed that the release of adsorption energy of interacting oxygen (O) and various other metals atoms, introduced significant disorder at GaAs surface layer. This produces local strain at oxide /GaAs interface and presence of various types of defects like antisites and vacancies were reported [14]. According to them the high density of surface states present around 0.8 eV below conduction band (CB), were due to As deficits possessing acceptor nature. Moreover significantly high donor nature surface states near valance band (VB), but relatively quite small in comparison with mid gap states, were caused by Ga deficit defects [14].

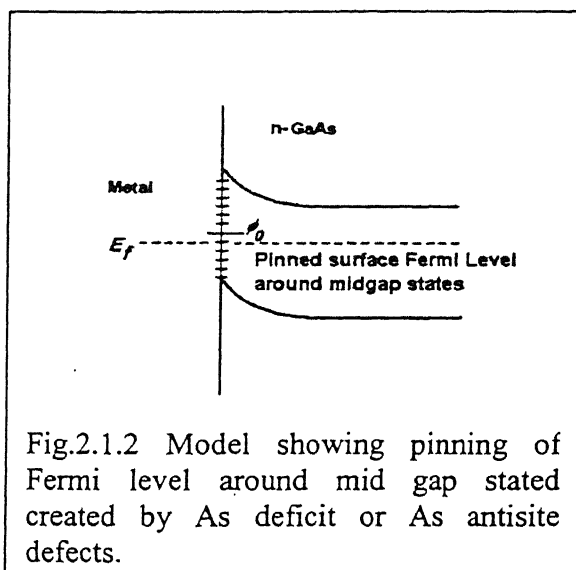
According to Besser et al. [19] surface states responsible for Fermi level pinning were introduced by arsenic (As) and gallium (Ga) antisite defects. They proposed that the singly and doubly ionized As antisites produced double donor level at 0.65eV and 0.9 eV

below CB, respectively, and Ga antisite caused double acceptor level near VB [18]. The pinning position of Fermi level was suggested to depend upon the equilibrium concentration of Ga and As antisites. They stated that the As rich surface, energetically more favorable at room temperature and which appeared after GaAs etching in acidic etchant, exhibited very high density of As antisite defects. These As antisites defects were not compensated by the small amount of Ga antisites present, due to which the Fermi level was pinned by As antisite defects [19].

The ensuing unified model that will be frequently used in this work is based on the review of the issue of surface states. There are mainly two sources of surface states in GaAs band gap. The first source is local strain present at oxide/GaAs interface, which exhibited parabolic distribution of surface states in band gap. The second source of surface states are As and Ga deficit-induced defects like antisites, vacancies etc. [14], which create high density of mid gap surface states (due to As deficits or As antisites) and relatively low density of surface states near VB (due to Ga deficits or antisites) [18,19]. Fig.2.1.1 shows the presence of surface states produced by local strain and these Defects.

The effect of above described surface states on surface band gap of GaAs is on a metal semiconductor junction having insulator film in between is shown in Fig. 2.1.2 It clearly shows the Fermi level pinning approximately at mid gap position. In order to eliminate these surface states from the energy gap, passivation should be capable of





removing oxides and deactivating antisite or As and Ga deficits defects. Moreover the passivant should not create surface states due to its own presence.

2.2 Surface Passivation of GaAs:

A large number of passivation schemes were employed to achieve unpinned Fermi level and surface state density at GaAs surface. The succinct list of major passivating elements and compounds comprises of Ga_2O_3 (Gd_2O_3) [21], nitrogen (N) [22], chlorine (Cl) [23], hydrogen (H) [24], polymerized thiophene [25,26], phosphorous [27,28], selenium (Se) [29], sodium diodecyldithiocarbamate (DODTC) [30], oxygen (O) [31,32], fluorine (F) [33,34,35] and most important of all sulfur (S) [36,37].

Kwo et al. [21] reported that the electron beam evaporation of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ garnet produced a mixed oxide film of $(\text{Ga}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ having $x\%$ of Gd_2O_3 . For $x \geq 14\%$ this film showed low leakage current, high break down strength and good surface passivation characteristics. The explanation adduced to define the passivation capabilities of $(\text{Ga}_2\text{O}_3)_x (\text{Gd}_2\text{O}_3)_{1-x}$ oxide layer was that Gd_2O_3 while exceeding 14% limit in oxide film either reduced the oxide vacancies or stabilize the 3^+ oxidation state of gallium oxide.

Nitrogen ion bombardment on GaAs (100) produced strongly bonded GaN layer on the surface. GaN film, whose thickness was a function of bombarding ion energy, exhibited reduction in surface depletion region. Bombarded nitrogen also reduced the excess As and lattice disorder to yield improved surface properties [22].

Chlorine was used for GaAs surface passivation. Lu et al. [23] reported realization of air stable Cl terminated GaAs surface, exhibiting improved surface electrical properties. GaAs was dipped in 10% HCl for few minutes to produce the Cl passivated surface. It was shown that GaCl bond was significantly more stable thermodynamically than As-Cl, Cl-H, and Ga-H bonds, due to which only GaCl bonds existed on GaAs surface after treatment.

Hydrogen passivation of GaAs surface, though extensively attempted in late eighties and early nineties from both experimental and theoretical-view points, could not produce effective and stable deactivation of surface states. Its low temperature stability precluded its application as a viable surface passivant [24].

Manorama et al. [25] have shown the passivation potentiality of plasma-deposited polymer film on GaAs surface. They observed that polymer thiophene film was capable of reducing surface states and surface barrier height significantly. The effectiveness of thiophene as a passivant was validated by PL, capacitance voltage (C-V) and Raman scattering measurements [26].

Richard et al. [27] have recently reported the phosphorous (P) base passivation of GaAs surface. It was carried out by two methods, by actuating exchange reaction on GaAs surface in tertiary butyl phosphine vapour ambience and, secondly by creating a direct thin GaP epitaxial layer. However the growth temperature was kept significantly high. Passivation thus achieved was found stable over several months. These findings were in close agreement with the results presented elsewhere [28].

Selenium (Se) has also been used as a passivant for realizing flat band condition for surface band gap GaAs [29]. However, this process involved high temperature annealing which placed a significant amount of Se in GaAs surface after replacing bulk associated As. It was believed that the overall change in atomic arrangement on/in the GaAs surface was the reason behind unpinning of surface Fermi level [29].

A low temperature surface passivation scheme was suggested for the fabrication of a surface passivating insulator film through electro-deposition of sodium diodecyldithiocarbamate DODTC [30]. PL and Raman measurement validated the effectiveness of this novel method and confirmed the reduction in charge depletion region and unpinning of surface Fermi level to a significant extent. X-Ray Photoelectron

Spectroscopy (XPS) study revealed that reactive sulphur present in DODTC, chemically bonded with surface As atoms to deactivate the surface state [30].

Surface passivation was also achieved by oxidizing GaAs surface through photo-oxidation method [31,32]. Oxygen dissolved in flowing de-ionized water (DI) was charged on GaAs surface in the presence of white light. It was found that Fermi level was still pinned though photoluminescence intensity (PLI) increased significantly. Based on the experiment and theoretical defect model it was suggested that the PLI enhancement was possible without decreasing the surface state density [20,31]. Further research apropos of mechanism of PLI was thoroughly explored and above concept was discarded. A discussion on this subject will be made under the Mechanism section of this thesis.

Ricard et al. [33] probed the passivation capabilities of gallium fluoride (GaF_3) on GaAs surface [33]. The GaF_3 film was directly deposited in a Molecular Beam Epitaxy (MBE) system. Electrical characterization of GaF_3/GaAs interface revealed the reduction in surface state density. Willston et al. [34] showed that fluoride ion (F^+) bombarded GaAs surface depleted surface As due to the formation of volatile arsenic fluorides. However, a gamut of fluorides comprises of GaF , GaF_2 , and GaF_3 were present on the GaAs surface. It was observed that the stability of these three fluorides differed with respect to temperature. GaF_3 dominated at low temperature while GaF was the major fluoride at high temperature. More interestingly the GaAs surface was completely devoid of fluorides around 300°C . These study are very helpful in understanding recent developments in the field of GaAs surface passivation utilizing F elements in conjunction with another passivant. According to Jeng et al. [35], a drastic improvement in electrical properties of GaAs surface were witnessed after applying a joint passivation scheme involving S and F passivants. GaAs treated in phosphorous sulfide/ammonium sulfide [$\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}$] and HF solution and followed by annealing at 300°C for 18 hrs showed a high degree improvement in electrical properties of GaAs surface while compared with individual treatment in $\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}$ and HF solutions. It was expected that the formation of sulphur fluoride such as SF_6 (having high binding energy of -291.8 kcal) was the most probable reason for this amelioration of electrical properties. However further research is required to create insight regarding the real mechanism of combined passivation. This

finding suggests that the opportunities exist for improvement in surface properties of GaAs utilizing more than one passivant [35].

Out of above-mentioned passivants sulfur is the most successful element in ameliorating GaAs surface quality. S significantly decreases surface recombination velocity [18] and increases the PLI [5,38]. Besides this surface barrier height become more sensitive towards metal work function [13,39] after quenching of major part of the active surface states by S on GaAs surface [40]. The science and methodology of S passivation has improved significantly in past few years due to the extensive theoretical [41-44] and experimental studies [45-64]. Complete realization of flat band energy gap, free from surface states, was reported using improved S passivation methods [39]. However, these improved S passivation techniques grossly depend upon processing at high temperature, $\sim 400^\circ\text{C}$, under ultra high vacuum (UHV) conditions [39,48-54]. Ensuing section is devoted to cover important aspects of S passivation methodologies, mechanisms, and other concerning factors from various viewpoints.

2.3 Sulfur passivation of GaAs:

Initially, S passivation was mainly carried out utilizing aqueous (aq.) solutions of sodium sulfide (Na_2S) [36, 37] and ammonium sulfide ($(\text{NH}_4)_2\text{S}$) (with or without dilution) [45-48]. Further improvement in S passivation effectiveness was noticed by using non-aqueous solvent to prepare sulfide solution for passivation [49-54]. A change in the S charging method from sample dipping to electrochemical S charging also showed clear improvement in electrical properties of GaAs surface [55-58]. In the quest for achieving stable S passivation and improved surface properties, many theoretical studies [43,44] and experimental work were carried out to determine high temperature characteristics of S passivated GaAs [39,59]. Results of these studies showed that Ga-S bonds on GaAs provided very stable S passivation without providing any extra surface state in the energy band gap [42,44]. However, the As-S bonds were observed to be remarkably less stable and inferior from the viewpoint of their electrical properties [43]. These facts prompted researchers to provide only Ga-S bonds on GaAs surface either by direct deposition [3,4,60] or by adding annealing treatment in addition to S passivation treatments [39,44].

2.3.1 Sulfur passivation methodologies

(a) Passivation by aqueous sulfide solution

The solution utilized were Na_2S (aq.) and $(\text{NH}_4)_2\text{S}$ (with or without dilution). The solution treatment to bring about surface passivation invariably start with surface cleaning (degreasing and deoxidation) of sample [36, 37]. The cleaned sample have been dipped in solution at room temperature [61] or slightly higher temperature [62] for several minutes to many hours [5]. Sometimes, the cleaned GaAs are spin coated with sulfide solution [63]. Two main drying operations have been reported for sulfide solution treated samples, spin drying [46] and N_2 drying [45]. The effects of processing parameters and solution characteristics of passivation properties are widely covered in ref. [10,64]. Here we will briefly discuss the effect of surface chemistry and temperature maintained during sulfidation. These two factors have major impact on final bonding types on S passivated surface of GaAs.

Deoxidation of GaAs surface is an important treatment before sulfide passivation because it decides the surface chemistry before S passivation on GaAs sample. It is well known that Ga atoms of GaAs surface are highly dissolvable in acids such as HCl , H_3PO_4 etc. and leave deoxidized As-rich surface after dipping GaAs sample in these acids [62]. However, ammonium hydroxide solution produces near stoichiometric GaAs surface free from elemental As (As^0) [10]. Depending upon the relative amount of As and Ga quantity of As-S and Ga-S bonds changes on S treated sample [64]. It was clearly shown that Na_2S (aq.) solution produced higher number of As-S bonds for a given As/Ga ratio while $(\text{NH}_4)_2\text{S}$ has a greater tendency to yield more number of Ga-S bonds than Na_2S (aq.) solution for a given As/Ga ratio [64,65].

Characterization of sulfide solution-passivated GaAs surface, revealed that the following information. Na_2S (aq.) and $(\text{NH}_4)_2\text{S}$ solution both increased the PLI [36]. However, it was reported that sodium sulfide treatment did not unpin the surface Fermi level [19] while $(\text{NH}_4)_2\text{S}$ do noticeable unpinning of surface Fermi level [66]. Sodium sulfide solution passivation was observed to be vary sensitive towards concentration of sulfide salt [67] while $(\text{NH}_4)_2\text{S}$ solution effectiveness was indifferent towards concentration factor [13]. S passivation effect vanished after thorough rinsing for both types of sulfide solution treatment [10]. Na_2S (aq.) and $(\text{NH}_4)_2\text{S}$ solution were effective in

reducing surface oxides, gallium oxide and arsenic oxides [36,62]. However, the dissolution rate of As° was significantly higher in $(\text{NH}_4)_2\text{S}$ solution to compared the with Na_2S (aq.) solution [46]. Sandroff et al. [37] noticed clear distinction between nature of bonding S and GaAs surface for both the solutions. It was suggested that Na_2S (aq.) solution provided As_2S_3 type compound on GaAs surface where S atom bridged between two As atoms while $(\text{NH}_4)_2\text{S}$ solution treated GaAs exhibited two S atoms staying between two As atoms [37]. The mechanism of surface passivation will be thoroughly discussed later. The aq. $(\text{NH}_4)_2\text{S}$ solution passivation produced superior electrical properties compared to aq. Na_2S passivation on GaAs surface.

(b) Passivation by non-aqueous sulfide solution

Sulfide solution treatment was more effective when sodium sulfide and ammonium sulfides were dissolved in solvent with lower dielectric constant [49]. However passivation methodology remain almost akin to aqueous sulfide solution passivation of GaAs surface. Properly degreased and deoxidized GaAs samples were immersed in non-aqueous sulfide solution at room temperature [49-51]. The residual solution was removed from the sample surface by spinning it at 1000 rpm all the time. The effectiveness of the application of non-aqueous solvents (alcohols of low dielectric constants such as ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) [$\epsilon = 25.3$], isopropanol ($i\text{-C}_3\text{H}_7\text{OH}$) [$\epsilon = 20.18$], tertiary butanol ($t\text{-C}_4\text{H}_9\text{OH}$) [$\epsilon = 12.47$]) were justified by PL, XPS and Raman scattering studies [49,38]. Results of PL and Raman studies are presented in Table 2.3.1.

Table 2.3.1: Results of PL depletion width (from Raman scattering study) and reactivity of S changing with dielectric constant of solvent used. Data were taken from ref. [38].

Passivation treatment in	Dielectric constant (ϵ)	PLI (a.u.)	Depletion width (nm)	Reactivity of S in solution (a.u)
No passivation	-	1.0	33.6	-
$(\text{NH}_4)_2\text{S}_x$	-	1.47	34.1	2.7
$\text{Na}_2\text{S} + \text{H}_2\text{O}$	80.10	1.50	33.9	6.0
$(\text{NH}_4)_2\text{S}_x + \text{C}_3\text{H}_7\text{OH}$	20.18	1.70	26.2	80
$(\text{NH}_4)_2\text{S}_x + t\text{-C}_4\text{H}_9\text{OH}$	12.47	2.00	24.9	165
$\text{Na}_2\text{S} + \text{C}_3\text{H}_7\text{OH}$	20.18	2.30	24.2	8000
$\text{Na}_2\text{S} + t\text{-C}_4\text{H}_9\text{OH}$	12.47	3.58	23.6	212000

These results showed that the reactivity of S in solution was a strong function of dielectric constant of the solvent. A decrease in the dielectric constant of solvent increased the reactivity of S in solution. The increase in PLI and decrease in depletion width indicate decrease in surface recombination velocity and unpinning of surface Fermi level from mid gap states. The simultaneous improvement in both of the electrical properties indicated overall change in surface states spectrum in energy band gap [38,49]. The performance of $(\text{NH}_4)_2\text{S}$ non-aqueous solution was inferior to the performance of Na_2S non-aqueous solution (alcoholic solution), when solvent of same dielectric constant was used [49], which has been explained by solution chemistry principal discussed elsewhere [51,52].

Remarkable changes in nature of surface bonds were also noticed during XPS study of non-aqueous Na_2S solution treated GaAs surface (Table 2).

Table 2.3.2: Relative intensity of peaks corresponding to various type of bonds, surface coverage in mono layers (MLs) observed in core level XPS study of gallium (Ga3d) and arsenic (As3d) on GaAs surface with changing value of solvent dielectric constant (ϵ). Data were taken from ref. [49].

Treatment	ϵ	As-O (a.u.)	As-S (a.u.)	As ⁰ (a.u.)	Ga-O (a.u.)	Ga-S (a.u.)	S (a.u.)	Surface Coverage (MLs)
Untreated	-	0.12	0	0.19	0.07	0	0	0
$\text{Na}_2\text{S}+\text{H}_2\text{O}$	80.13	0.07	0.04	0.14	0.05	0	0.04	0.4
$\text{Na}_2\text{S}+\text{C}_2\text{H}_5\text{OH}$	25.30	0.05	0.06	0.19	0.02	0.04	0.10	0.8
$\text{Na}_2\text{S}+\text{C}_3\text{H}_7\text{OH}$	20.18	0.02	0.09	0.19	0.02	0.03	0.12	1.3

The data in Table 2.3.2 clearly shows that oxides removal and sulfur coverage was significantly better with non-aqueous Na_2S solution compared to aqueous solution. Excess As (As⁰) removal was poor in case of non-aqueous Na_2S , but helped in justifying that elemental As⁰ do not play any role in S passivation [10]. It was also observed that formation of Ga-S bonds had also become possible by the utilization of alcoholic solvent [49]. The mechanism of S passivation will be presented later.

(c) Electrochemical S charging

Electrochemically charged S produced superior quality surface passivation over normal sulfide solution passivation [55-58]. In order to achieve surface passivation, the following methodology was adopted. After degreasing and deoxidation, as discussed for aqueous sulfide solution passivation methodology, the GaAs sample were so placed in a Teflon holder [55] or in a wax case [56] such that only one face of GaAs sample is exposed to S containing electrolyte. Ohmic contact was established with the surface to be passivated prior to fixing the sample in the electrochemical cell [39]. Different types of S containing electrolytes were used: Na₂S-ethylene glycol [57], (NH₄)₂S solution [57,57], solution obtained from sequential mixing of propylene glycol with ammonia and hydrogen sulfide (H₂S) [56]. Supplying anodic current in milliamps [55] or microamps range [6] for few minutes charged sulfide ions. In the electrochemical cell the counter electrode used were metal plate [55] and Pt [56]. The electrochemically charged GaAs surface was rinsed in ethanol and then blown in dry nitrogen gas by one research group [56].

XPS studies of electrochemically charged GaAs surface showed the presence of gallium sulfides (Ga₂S₃, GaS) and arsenic sulfide (As₂S₅) on it [56]. The passivation film, thus produced, was capable of providing a more stable deactivated surface in comparison with passivation film produced by ordinary sulfide solution treatment [55]. Moreover electrochemical S passivation was significantly stable against water rinsing [57]. Presence of stable GaS and As₂S₅ (As⁵⁺ state) were mainly responsible for the improvement in properties of electrochemically S passivated surface [57]. Additionally it is well established that As in higher oxidation state provides better interface properties compared to As³⁺ state [55].

(d) Deposition of GaS

The superior properties of Ga-S bonds on GaAs surface [43], prompted researches to deposit GaS directly on suitably reconstructed surface [52]. Realization of this process necessitated the availability of highly controlled systems and high substrate temperature to maintain required surface reconstruction and surface chemistry.

Direct deposition of GaS was successfully carried out by using gallium cluster ((t-Bu) GaS)₄) as a single source precursor in ultra high vacuum conditions of MBE system [4,8,60]. The substrate was cleaned by trisodium ethylaminoarsinic (TDMAAS)

and Bisdimethyl aminochloroarsinic (BDMAASCl) [4]. During deposition of pure GaS, precursor cell was maintained at 120°C [4,8]. The substrate temperature was kept in 350°C to 500°C temperature range. The substrate was at high temperature because it was essential to produce the required surface reconstruction, which played an important role in deciding extent of improvement in electrical properties of GaS/GaAs interface. For instance, As rich (4x4) surface reconstruction produced 5×10^{10} eV/cm² surface states [4] while As rich (2x4) surface reconstruction yielded 1.8×10^{11} eV/cm² density of surface states [8] at GaS/GaAs interface.

The deposited GaS film was reported to be amorphous in nature and exhibited excellent surface morphology [4]. The GaS/GaAs interface exhibited excellent electrical properties only when the GaS film thickness was on the lower side, since excess amount of GaS produced high interface strain. The high lattice strain, present at interface facilitated conversion of film nature from amorphous to polycrystalline, with a high density of dislocation density [4]. Moreover the GaS film behaved like an insulator because it had a bond gap of 3.5 eV [8]. Deposition of GaS produced impressive enhancement in PLI and almost flattening of energy band gap near surface. The passivation was also tested to be stable for at least two years [4].

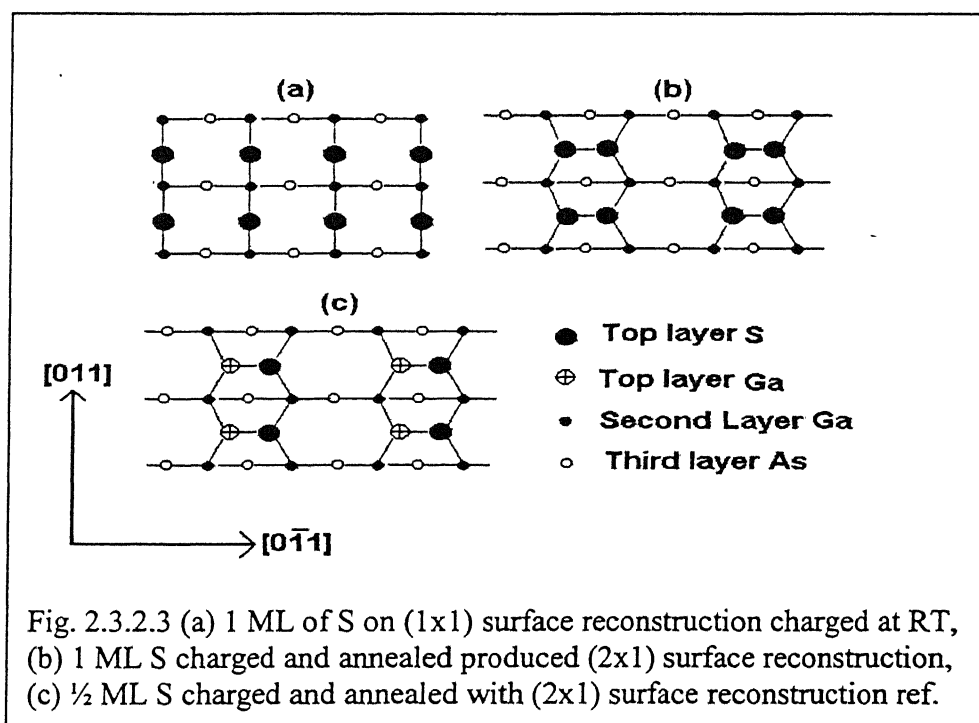
(e) S passivation followed by annealing

Moriety et al. [39] used the following scheme to achieve almost complete unpinning of surface Fermi level in energy gap [39]. First the As-capped GaAs (100) samples were indium bonded to a tantalum or molybdenum holder before inserting the sample in UHV system. In the UHV system As decapping was carried out at 350°C. The As decapped samples were heated in 400-570°C range of temperature to produce c(2x8) As rich surface reconstruction and near stoichiometric (4x1) surface reconstruction. Thoroughly cleaned samples with c(2x8) and (4x1) starting surface reconstruction, were charged with molecular beam sulfur in an electrochemical cell. An anodic current of 0.5 mA was maintained for 5 minutes at room temperature. The sulfur charging step was followed by an annealing treatment from 450-500°C which yielded (2x1) surface reconstruction. XPS study of these samples confirmed the unpinning of surface Fermi level for sample with (4x1) surface reconstruction [39].

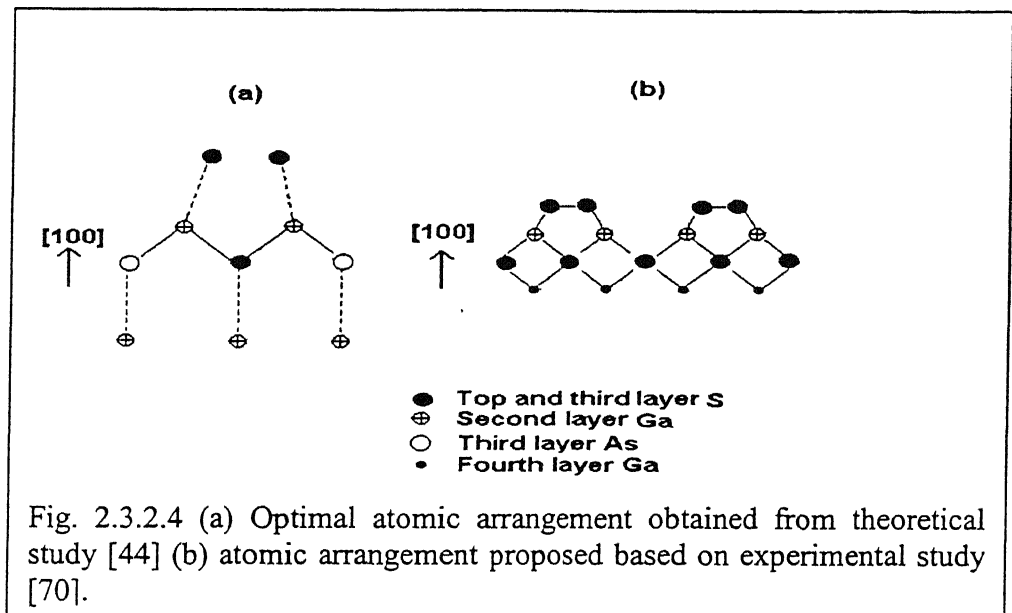
It was shown that unpinning for (4x1) surface reconstruction was due to optimum atomic arrangement caused by S passivation and annealing. It was also shown that S atom had successfully replaced the bulk-associated surface As atoms, which was in agreement with the findings presented elsewhere [59,68]. More importantly the resultant atomic arrangement contained Ga-S bonds on surface layer attached with partially or completely replaced bulk associated As [39,69]. This experimental finding is in good accordance with atomic arrangement, predicted for (2x1) reconstructed S passivated surface [44] for engendering complete unpinning of surface Fermi level. In the case of c(2x8), arsenic rich GaAs surface, it was found that replacement of bulk-attached As at surface with S was not carried out significantly after annealing of S passivated sample [39]. This method again was energy intensive and require a high degree of control.

2.3.2 Atomic arrangement and surface reconstruction of passivated surface

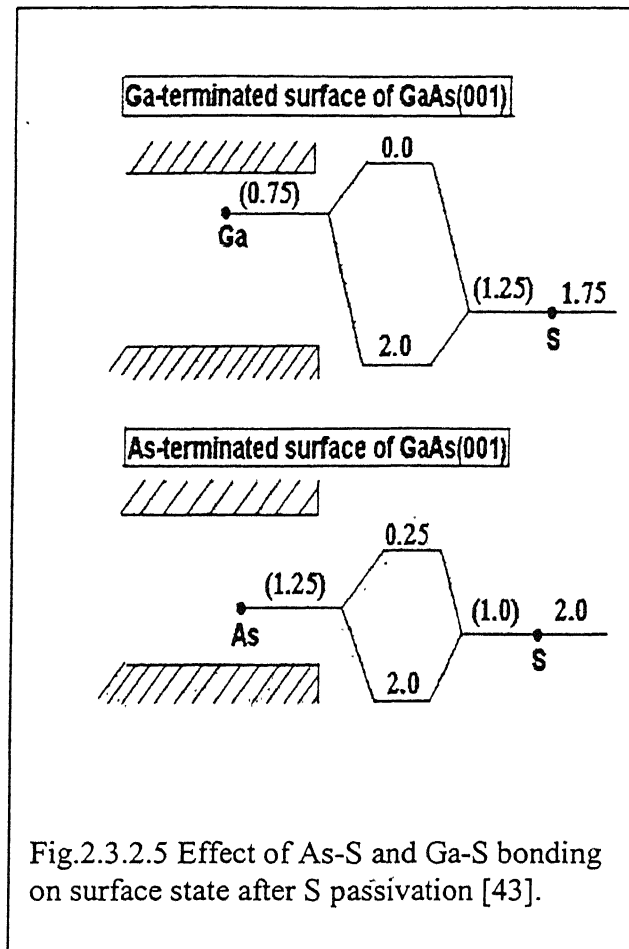
Atomic arrangement of S passivated surface mainly depended upon S coverage and availability of activation energy [40]. Three types of surface bonds, As-S, Ga-S and S-S affects the surface state density in energy band gap [43]. The As-S bonds formation required lesser activation energy than that of Ga-S. The number of As-S and Ga-S, S-S



bonds were found to be increasing with S coverage. More importantly existence of bonds S-S bonds is strongly dependent on availability of S on GaAs than As-S, Ga-S [37]. It was observed that S attached to As-S bonds releases itself upon increasing temperature and did not leave the GaAs surface until temperature was high [56]. Freed S atoms in turn made bonds with surface Ga atoms and simultaneously start replacing bulk associated As atoms [59,68]. According to the theoretical calculation, replacement of alternate bulk associated atoms by S on surface with (2x1) reconstruction and Ga-S surface bonds is the optimal atomic arrangement for the realization of flat band condition which significantly matches with the atomic arrangement conceived based on experimental studies [39] Fig.4. Main difference is in extent of removal of bulk associated As from the surface layer.



The impact of the presence of above described bond on energy band diagram is following. First principle study suggested that As-S bond contained 2.25 electrons while for strong bonding 2 electrons are needed, presence of excess 0.25 electrons, present in antibonding level weaken this bond. However Ga-S bond contained exactly 2.0 electronic level was due to the partially filled antibonding states of As-S bond. Whereas no level appeared in energy band gap due to Ga-S bond possessing completely filled electrons bonding state and completely vacant antibonding state.



Electrical properties of S-passivated GaAs surface depend upon the final surface chemistry and atomic arrangement on the surface [39,44,72-74]. There exist significant differences in the nature of surface reconstruction and type of bonding after low-temperature sulfide solution passivation ($T < 100^\circ\text{C}$) and high-temperature sulfide passivation schemes. In near-room temperature sulfide passivation, surface chemistry mainly depends upon the type of methodology used [10,37].

In the case of low temperature S passivation methods, sodium sulfide passivation mainly produced As-S type bonds on Ga terminated surface Ga-S, As-S and S-S bonds were observed after $(\text{NH}_4)_2\text{S}$ based sulfide treatment Fig. 2.3.2.6 [37].

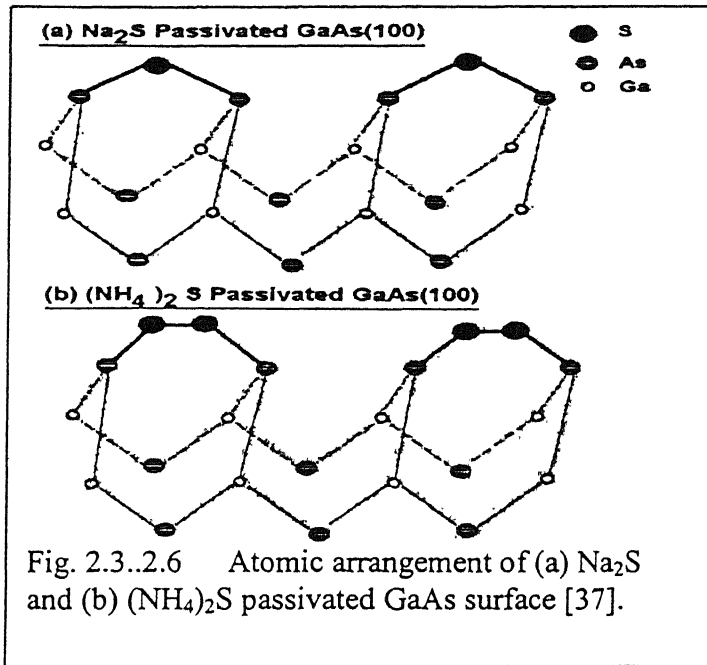


Fig. 2.3.2.6 Atomic arrangement of (a) Na₂S and (b) (NH₄)₂S passivated GaAs surface [37].

The models presented in Fig. 3 for (NH₄)₂S treated GaAs, have not incorporated the presence of Ga-S bonds, which were evidently present on ammonium sulfide treated GaAs surface [37]. Presence of Ga-S bonds, along with As-S bonds, was validated by an XPS study conducted on non- aqueous (NH₄)₂S solution treated GaAs surface [51]. It is quite apparent that there exists a need for a more complete atomic model that must include As-S and Ga-S and As⁰ (refer Table2).

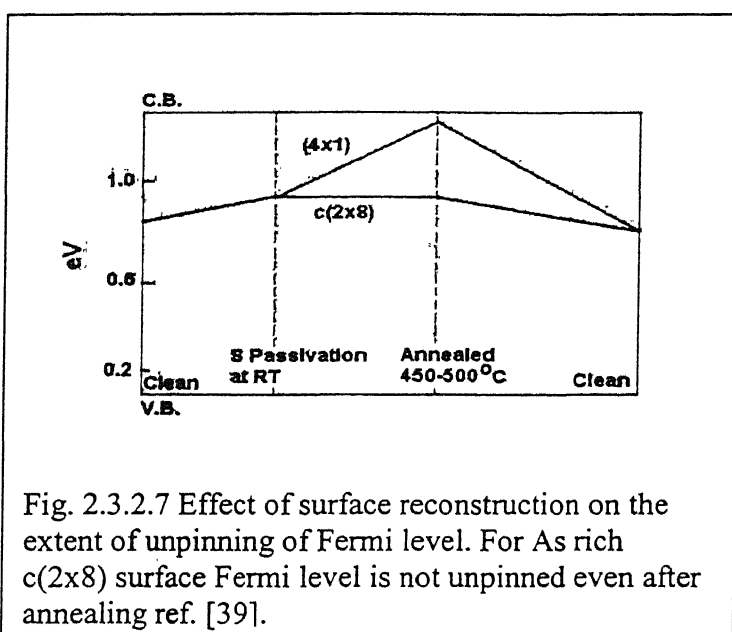
Surface reconstruction, after room temperature S passivation of GaAs surface, was theoretically estimated to be (1x1) [43]. Though it matched with LEED results recorded on room temperature (RT) H₂S passivated GaAs surface [68], it significantly differed from actual surface reconstruction (2x2) observed on (NH₄)₂S treated surface [75,76]. Reason for this difference was the amount of S released by H₂S and (NH₄)₂S during passivation.[38,69].

Electrochemical S passivation of GaAs surface evidently produced gallium sulfide (Ga_2S_3) and arsenic sulfide (As_2S_5) which were in higher oxidation state than gallium sulfide and As_2S_3 formed during simple sulfide solution treatment. [55,56]. Electrochemically passivated GaAs exhibited superior electrical properties and higher stability in comparison with normal sulfide passivation [55]. No appropriate atomic model was suggested for electrochemically-passivated GaAs surface.

Close control over S passivation parameters becomes very necessary when efforts for realizing optimum atomic arrangements for complete unpinning of surface Fermi level. In order to grow thick GaS film on suitably reconstructed GaAs surface, controlled environment of MBE system and high substrate temperature was employed [45]. By maintaining the substrate temperature in the 350-500°C range, As-rich surface reconstruction such as $c(4\times4)$ [4] and (2×4) [48] were established. On these surface GaS was deposited to provide excellent electrical properties at interface [3]. The choice of depositing GaS film, and not arsenic sulfide film, on GaAs surface was based on Ga-S superior electrical properties and stability over As-S as discussed earlier [15,43]. GaS bonds are found to be stable up to $\sim 530^\circ\text{C}$ [77], while As-S bonds vanished before reaching 300°C [77,78].

Another energy intensive passivation method in which S passivation was followed by annealing successfully produced surface energy gap with unpinned Fermi level [39]. This method, apart from producing GaS on the surface, also replaced a significant amount of substrate associated As atoms with S. This treatment yielded (2×1) surface reconstruction on S passivated surface [39]. Atomic model of S passivated and annealed surface [70,76] was in close agreement with the result of theoretical study [44] as shown in Fig. 4. The major difference in atomic models conceived based on of experimental and theoretical study, was in extent of substrate associated As replaced by S [59]. Suitable experimental studies are required to sort out this issue.

Moriety et al. [39] clearly showed the importance of starting surface chemistry and surface reconstruction. It was reported that As rich c(2x8) GaAs surface Fermi level remain unpinned due to inadequate Ga-S bonds formation and paucity of surface As atom replacement with S. Moreover As dimer, which themselves create extra electronic states in energy gap, were also present after sulfidation and annealing treatment on surface



c(2x8) reconstruction. Fig.7 shows that near stoichiometric GaAs surface with (4x1) surface reconstruction was observed with completely unpinned surface Fermi level after the same S passivation followed by annealing treatment [39].

Another surface reconstruction (2x6), which is also considered to be stable one, was reported to have five S dimers in a unit [79-81]. On heating this dimer row breaks out the middle to yield (2x3) surface recombination [70]. Several researchers also showed that S passivated and annealed GaAs also had a tendency to acquire S dimer attached with Ga atom [69,70]. According to different studies, S dimer gave one electron to Ga atom to provide stable and neutral atomic arrangement on passivated surface [92]. Another important aspect of S passivated GaAs surface is the direction of dimers present on it [82,83]. S and As dimers are observed to be oriented in $[1\bar{1}0]$ direction on S passivated and annealed around 450°C. Heating beyond 550°C, eliminated S and As dimers and gave rise to Ga dimers oriented in the $[110]$ direction [82].

2.3.3 Mechanism of S Passivation

Several opinions exist on S passivation mechanism. Sandroff et. al. claimed that formation of protective As_2S_3 phase was the basis of S passivation [11,37]. Another group of researchers suggested that amelioration of surface electrical properties were due to the band bending resulting from sulfide solution treatment [18,36]. According to Haesgawa et al. sulfide treatment created fixed negative charge near the surface, which improve the surface properties [35,84]. The most popular concept of S passivation is based on reduction in surface state density [51,52].

The idea that As_2S_3 was the basis of S passivation was refuted by the findings presented in ref. [10]. In which two different S containing solutions gave equal enhancement to PLI even when As_2S_3 phase was absent in one case. Besser et al. claimed that the band bending was induced by sulfide solution on GaAs surface, which pushed the electrons away from the surface or surface states affected region. The increase in PLI was seen even when Fermi level was still unpinned due to this reason [18]. Large number of references showed that the increase in PLI and Fermi level unpinning were observed after sulfide solution treatment form the basis for the denial of the latter theory [51,67]. Haesgawa et al. [84] claimed that the increase in PLI was possible without decreasing surface state by the negative charge created by sulfide treatment on GaAs surface. Experimental studies on S passivation shows that the source of surface states always decreased to small or great extent after passivation treatment [46,60]. On this basis the concept of Haesgawa et al. was found to be inconsistent with existing experimental results.

Aqueous Na_2S solution improved PLI but Fermi level remain unpinned [19]. However, when non-aqueous Na_2S solution was used for S passivation, unpinning of Fermi level was observed along with an increase in PLI [49,51]. It suggested that in the former case only a small part of surface state was reduced but in the later case the surface state reduction was significantly large. XPS results confirmed that the sources of surface states were greatly reduced by the non-aqueous sulfide treatment [49].

Low-temperature sulfidation is limited by the formation of As-S bond, which creates surface states within the band gap [43]. Ga-S bond is more stable and do not

produce extra surface states after passivation [75]. In order to harness the superior properties of Ga-S bond, the following two schemes were employed. First, direct deposition of GaS on suitably reconstructed As rich surface in controlled UHV conditions was carried out [4,8]. While in other case annealing treatment was added with S passivation of GaAs [39].

Direct deposition of GaS from suitable precursor on a substrate, kept at high temperature in UHV, yielded extremely low surface state density at the interface. As there was no oxygen in the system, only termination of dangling bond on reasonably good surface with already low surface states density, was left. Deposition of GaS deposition effectively passivated these remaining surface states to an extent that almost complete band bending was eliminated [4].

Sulfidation followed by annealing also yielded nearly flat band condition due to the following facts. Annealing treatment, apart from producing GaS bonds on the surface also replaced the surface associated As atoms with S [59] to some extent to produce a very stable and electrically inert atomic arrangement [44]. For this passivation treatment final surface chemistry determined by the XPS which was in close agreement with theoretically calculated surface chemistry for the complete unpinning of surface Fermi level from the mid-gap states.

Reduction in surface states density greatly depends upon methodology. S passivation relies on high temperature treatment in highly controlled environment for complete unpinning of the Fermi level.

2.4. Present research trends: The most successful sulfur passivation methods required very controlled environment and annealing as an essential step in passivation scheme. Due to which it is very difficult to assimilate the method into device fabrication routine. A low temperature and surface passivation method for the production of deactivated stable GaAs surface is the field of thirst.

Recently few works has been reported regarding the use of more than one reagent to produce better surface electrical properties than single reagent sulfur passivation. Jeng et al. [35] showed that the effectiveness of using both phosphorous sulfide/ ammonium sulfide ($P_2S_5/(NH_4)_2S_x$) solution and hydrogen fluoride (HF) solution on the barrier height enhancement of Ag/n-GaAs Schottky diode. A clear improvement in barrier

height, more than single reagent sulfide passivation was exhibited. Researches has also shown that sulfide passivated GaAs manifested additional PLI enhancement after hydrogen annealing of already passivated GaAs surface. Furthermore GaAs treated with sulfide solution followed by metal salt solution produced air stable surface passivation which remained significantly stable for more than a year time. However all the steps of this combined passivation were executed at room temperature in ambience. The ability of combined surface passivation to produce superior surface electrical properties and more stable surface passivation has drawn considerable of researchers in this direction. This rather new stream of surface passivation is promising to yield more efficient, cost effective less time consuming

Experimental Procedure

Surface passivation of GaAs surface was started with silicon nitride deposited n-doped GaAs samples. Samples for passivation studies were thoroughly cleaned and/or metallized and then passivated in freshly prepared sulfide and fluoride solutions under different schemes either by simply dipping in salt solution or electrochemically. Following section discuss the various steps of sample preparation and the details of the characterization method adopted for evaluating the surface passivation.

3.1 Preparation of silicon nitride deposited n-doped GaAs samples and their further characterization:

Silicon (Si) implanted GaAs (001) wafers, deposited with silicon nitride (SiN), were prepared from the semi insulating (SI) GaAs, grown at American Xtal Technology USA. In order to make SI-GaAs conducting, Si implantation was carried in two stages, the first N- channel doping stage and the second N+ ohmic contact stage, see Table 3.1.1. Thereafter the dopants were activated by appropriate annealing treatment. Electrochemical C-V data for dopant concentration versus depth file was provided with wafer according to which SI-GaAs was doped up to 0.42 μ m deep out of the total 0.66mm wafer thickness. Concentration profile of Si dopants was obtained from electrochemical C-V measurement Fig.3.1. Sheet resistance measurement of these samples was also carried out after this stage.

In order to achieve the modified Si dopant concentration near the surface region etching was carried out by dipping samples in $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ (1:1:98) solution for several minutes as specified in Table 3.1.1. The sheet resistance was again measured by four-point probe after etching treatment. In next step GaAs surface was deoxidized in NH_4OH for 5 min and then plasma enhanced chemical vapor deposition (PECVD) of silicon nitride was carried out in PLASMATHERM-790 CVD chamber. Deposition was carried out at 250°C by maintaining silane to ammonia ratio at 1:2 and overall gas pressure at 450 mm Torr. PECVD grown silicon nitride possessed hydrogen (H) in it. The non-stoichiometric composition of SiN film was represented by SiN_xH_y . Auger electron spectroscopy (AES) carried out by another group on similar PECVD silicon nitride reported the Si/N ratio to be 1:1.24.

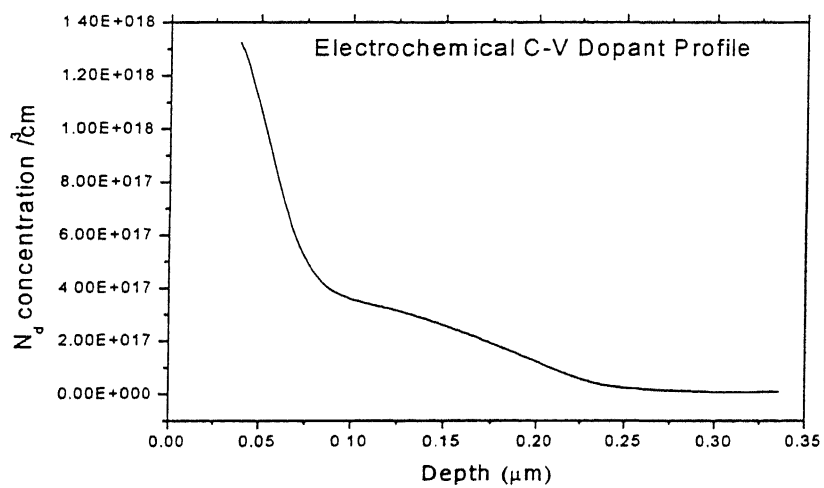


Fig. 3.1 Electrochemical C-V silicon dopant profile in implanted GaAs sample.

Thickness and refractive index were measured with the help of Rudolph Research-AutoEL2 ellipsometer. Sample specific details are provided in Table 3.1.1.

Table 3.1.1: Sample designation (W#) with implantation details, etching time, sheet resistance (σ) before and after etching, thickness and refractive index (ϵ) of SiN film.

S.No.	W #	First implantation dose (N-channel doping stage)	Second implantation dose (N+ ohmic contact stage)	σ Ω / cm^2 (before etch)	etching time (min)	σ Ω / cm^2 (After ss etch)	SiN film thickness (\AA)	ϵ
1	18	$5.2 \times 10^{12} / \text{cm}^2$ at 180keV	$1.0 \times 10^{13} / \text{cm}^2$ at 30 keV	~ 236	2	615	196	1.856
2	20	Do	Do	~ 236	2	601	196	1.856
3	21	Do	Do	~ 236	NA	NA	192	1.870
4	22	Do	Do	~ 236	NA	NA	192	1.870
5	4	$5.3 \times 10^{12} / \text{cm}^2$ at 180keV	$1.5 \times 10^{13} / \text{cm}^2$ at 35keV	199	1	331	102	1.851
6	5	Do	Do	206	1	354	235	1.890
7	6	Do	Do	208	1	365	293	1.904
8	7	Do	Do	204	1	349	393	1.923

Further experiments were conducted at IIT Kanpur to characterize SiN film. Rutherford back scattering (RBS) was carried out to obtain the Si/N ratio of SiN film present on GaAs. For this study 2 MeV Van de Graaff accelerator was used while detector was placed at 30 from the line of incident positive-helium (He^+) ion beam. The effective charge induced in the sample by the bombarding He^+ ion beam was found to be 5-10 nA. The Si/N ratio from RBS results was determined to be 1:1.38 whereas the result of earlier AES studies carried out to determine Si/N ratio revealed it to be 1:1.24. For this study wafer no. 18 was used. The thickness of SiN film was also determined from RBS spectra, which was 250 \AA . The thickness of silicon nitride

film was determined by transmission electron microscopy (TEM). Sample preparation for TEM study was carried out in following steps.

Step1: First, two strips were cut from the wafer and were joined by putting

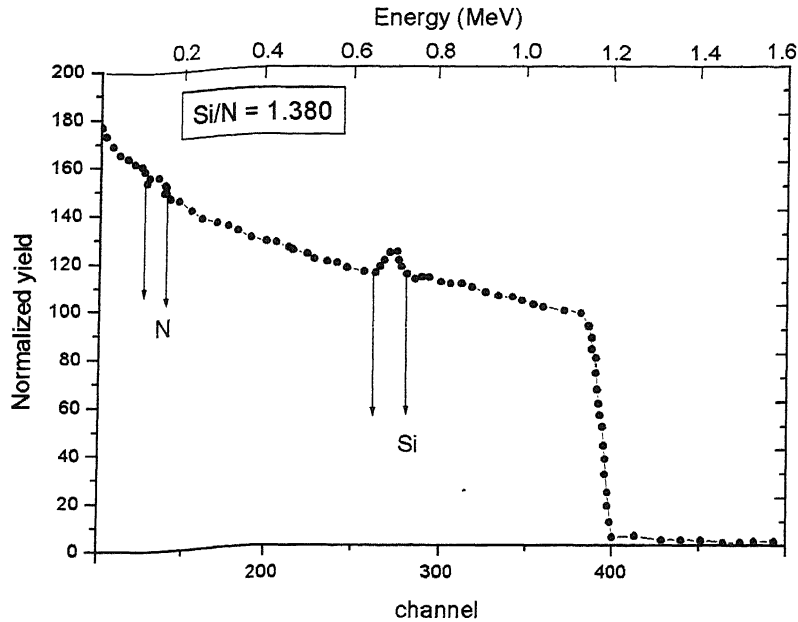
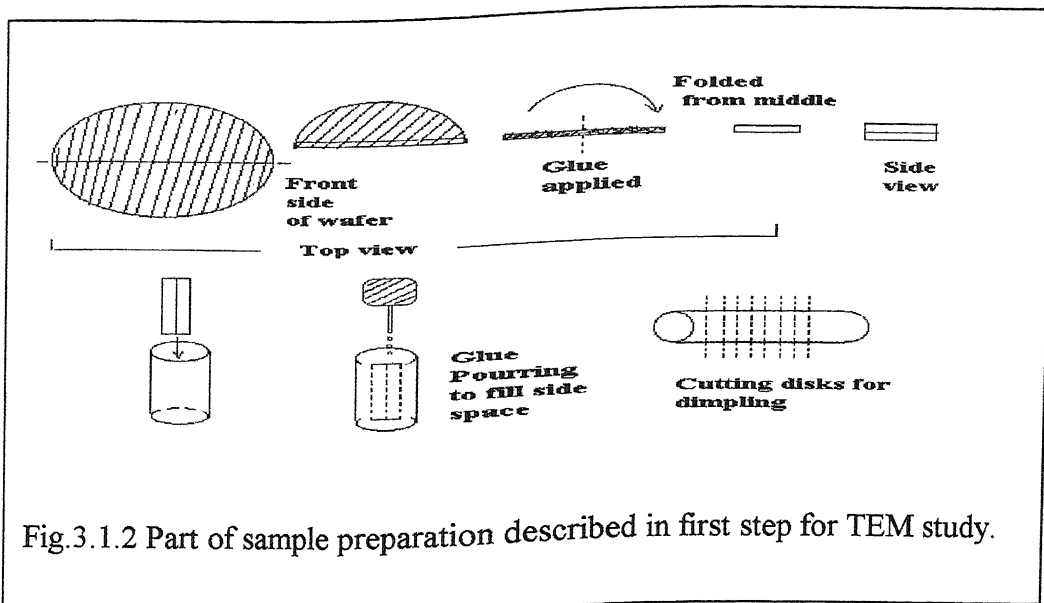


Fig.3.1.1 RBS spectra of SiN film deposited on n-GaAs (w# 18) showing the presence of Si and nitrogen and this corresponding hump widths, which are directly proportional to the relative amount of Si and N in SiN.

glue on their front (SiN film side) so that the SiN films present on both the strips, are sandwiched. Glued strips were inserted in stainless steel tube and same glue was poured in this tube to fill the air gap between joined strip and tube wall to bond these strips with tube wall and was allowed to settle for 24 hours. Whole process discussed under first step is also shown through schematic diagram in Fig.3.1.2

Step2: Disks of 200 μm thickness were cut from this tube and was ground at the center position by dimpler machine in order to thin down central region to $\sim 20 \mu\text{m}$.

This



dimpling operation was carried out on either side of disk concentrically.

Step3: In this stage, dimpled disk was put in Ion Beam Miller for further thinning for six hour. Extreme care was exercised in taking off sample from miller to sample holder.

Step4: Finally adequately thinned sample was mounted in TEM and film thickness was estimated. It was measured to be 250 Å, which was approximately 65Å more than the value of thickness measured by ellipsometry Fig. 3 shows the pictures recorded during TEM study.

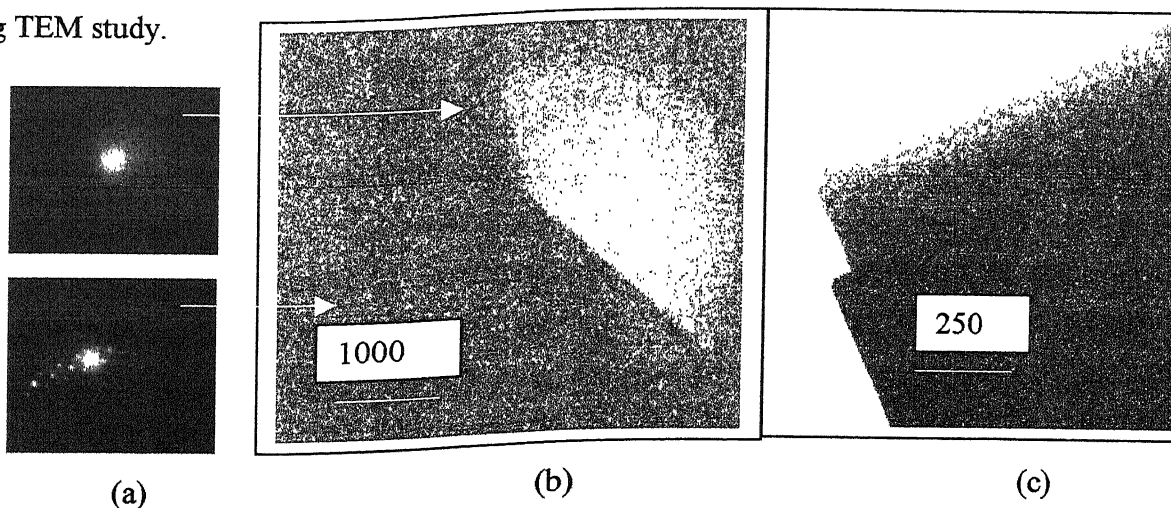


Fig. 3.1.3 TEM pictures taken from the cross-section of GaAs/SiN film at during thickness measurement. (b) SiN film at 12,000 X, (d) SiN at 80,000X, (a) diffraction pattern showing GaAs and diffraction pattern of epoxy film.

The attempts to estimate amount of hydrogen in PECVD SiN_xH_y by Fourier Transform Infrared Spectroscopy (FTIR) was unsuccessful.

Wafer number 5 was utilized for hybrid passivation utilizing both S and F passivants, and electrochemical sulfide passivation treatments. First, the SiN film was etched off by using diluted buffer hydrofluoric (BHF), $\text{BHF}:\text{H}_2\text{O}$ (1:10) solution for five min. BHF solution was prepared by mixing one part of NH_4F solution (1Kg NH_4F /1.5 liter distilled water) with 10 part of distilled water at room temperature. Etch rate of this solution was 2000 Å/min as determined by another group.

3.2 Experimental procedure: First stock solutions, containing passivating ions, were prepared followed by sample preparation and then surface passivation.

3.2.1 Stock solution preparation: The stock solutions, Na_2S and NH_4F salt solution, used for passivation was prepared in following manner. Saturated Na_2S salt solution was prepared in tert-butanol ($\text{t-C}_4\text{H}_9\text{OH}$). An excess of Na_2S salt was added in t-butanol and then this mixture was heated at 55°C for 5 min so as to bring sufficient amount of S in solution. Thereafter, the solution was allowed to cool down to room temperature. Two NH_4F solutions were prepared to see the effect of dissolved Fluoride ion concentration on surface passivation because solvent t-butanol can dissolve only very small amount of NH_4F whereas water can dissolve large amount of it. First solution was prepared by dissolving surplus amount of NH_4F in butanol and then heating at 55°C for 5 min to make this solution supersaturated. Thereafter solution was allowed to cool down to room temperature. The second solution of NH_4F was prepared by dissolving 100 gram of this salt in 150 ml deionized water (DIW) at room temperature. In order to determine the fluoride ion concentration in butanol, SPADNS (Sodium 2-Parasulfophenylazo 1,8-Dihydroxy 3,6-Napthalene diSulfonate) calorimetric method was utilized. In this method 50 ml sample solution was mixed with 5 ml SPADNS solution and 5 ml of Zirconyl Acid reagent followed by proper mixing of these solutions. The absorbance of 570 nm light was determined with the help of spectrophotometer. The concentration of fluoride ions was directly obtained from the standard graph of absorbance versus concentration. The

fluoride ion concentration was determined to be 0.72mg/liter. However the aqueous NH_4F solution has 0.222 Kg/liter, that is very high in comparison with first non-aqueous solution. The sulfide ion concentration in non-aqueous Na_2S /t-Butanol solution was determined by Iodometric method. In this method sufficient amount of iodine solution with concentration more than the sulfide ion concentration in the sample to be studied was taken in a conical flask followed by addition of 2 ml 6 N HCl solution. The 200-ml of sulfide solution was added to the above-prepared solution and change in color was observed. The complete disappearance of iodine solution color indicates the need for the addition of some more quantity of iodine solution in order to retain its color once sulfide solution sample has been mixed. This mixture of solution was back titrated with sodium thiosulfate and starch indicator till the end point is achieved. The concentration of sulfide ion was calculated by following formulas:

Calculation;

$$\text{Sulfide in mg/L} = \frac{A \times B - C \times D}{16000} \times \text{ml of sample}$$

where A=ml of Iodine

B= strength of Iodine solution

C= ml of sodium thiosulfate

D= strength of Sod. Thiosulfate

The sulfide ion concentration was determined to be 105 mg/Liter.

3.2.2 Sample preparation:

degreased and deoxidized prior to passivation treatment. A three steps degreasing or organic cleaning was performed by dipping the samples sequentially in trichloroethylene (TCE), acetone and methyl alcohol beakers. The beakers were kept in ultrasonic bath for 2 min during cleaning GaAs sample in each solvent. The degreasing operation was followed by rinsing of GaAs samples in DIW. The deoxidation of GaAs samples was performed next in $\text{HCL}:\text{H}_2\text{O}$ (1:4) solution for two minutes at room temperature and then rinsing in DIW. Subsequently, these samples were used for passivation in sulfide and fluoride solutions.

3.2.3 Passivation:

Wafer number 5 was utilized for all the passivation studies. Surface passivation of GaAs was carried out using non-aqueous $\text{Na}_2\text{S}/t\text{-Butanol}$, non-aqueous $\text{NH}_4\text{F}/t\text{-Butanol}$ and aqueous $\text{NH}_4\text{F}/\text{H}_2\text{O}$ solutions. During passivation either room temperature or 55°C was maintained. Mainly following two passivant charging methods, first by sample dipping in fluoride/sulfide solution and the second electrochemical charging of the passivants, were employed. All the passivation schemes used in present work can be broadly divided in two categories, first single step passivation using only one passivant and second double step passivation using two passivants. All the surface passivation schemes were designated with particular name showing sequence and type of passivant charged from particular solution Table1.

Table3.2.3.1: Typical passivation conditions for particular surface passivation scheme and symbols assigned.

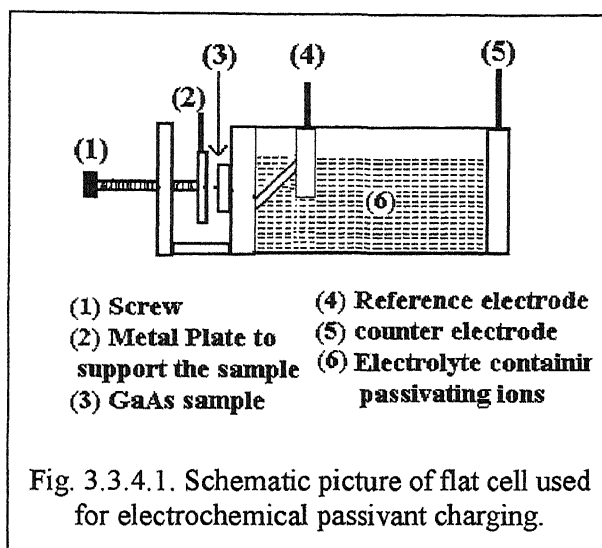
S. No.	Type of solution(s) containing passivant(s) in the order of their use, passivation temperature and passivant charging method.	Symbol
1	$\text{Na}_2\text{S}/t\text{-Butanol}$, RT or $T=55^\circ\text{C}$, dipping sample in solution	S_{NA}
2	$\text{Na}_2\text{S}/t\text{-Butanol}$, $T=55^\circ\text{C}$, dipping sample in solution	$S_{\text{NA}55}$
3	$\text{NH}_4\text{F}/t\text{-Butanol}$, $T=55^\circ\text{C}$, dipping sample in solution	F_{NA}
4	$\text{NH}_4\text{F}/\text{H}_2\text{O}$, RT, dipping sample in solution	F_{A}
5	$\text{Na}_2\text{S}/t\text{-Butanol}$, RT or $T=55^\circ\text{C}$, dipping sample in solution in the presence of ultrasonic vibrations	US_{NA}
6	$\text{Na}_2\text{S}/t\text{-Butanol}$, RT, Electrochemical charging of passivant	ES_{NA}
7	$\text{NH}_4\text{F}/t\text{-Butanol}$ followed by $\text{Na}_2\text{S}/t\text{-Butanol}$ solution $T=55^\circ\text{C}$, sample dipping in solutions	$F_{\text{NA}}S_{\text{NA}}$
8	$\text{NH}_4\text{F}/\text{H}_2\text{O}$ followed by $\text{Na}_2\text{S}/t\text{-Butanol}$ solution, RT, sample dipping in solutions	$F_{\text{A}}S_{\text{NA}}$
9	$\text{NH}_4\text{F}/\text{H}_2\text{O}$ followed by $\text{Na}_2\text{S}/t\text{-Butanol}$ solution, RT, Electrochemical charging of both F and S from respective solution	$EF_{\text{A}}S_{\text{NA}}$
10	$\text{Na}_2\text{S}/t\text{-Butanol}$ followed by $\text{NH}_4\text{F}/t\text{-Butanol}$ solution $T=55^\circ\text{C}$, sample dipping in solutions	$S_{\text{NA}}F_{\text{NA}}$
11	$\text{Na}_2\text{S}/\text{H}_2\text{O}$ followed by $\text{NH}_4\text{F}/t\text{-Butanol}$ solution RT, sample dipping in solutions	$S_{\text{NA}}F_{\text{A}}$
12	Passivation in single solution prepared by dissolving both Na_2S and NH_4F reagents in $t\text{-Butanol}$, $T=55^\circ\text{C}$, sample dipping in solution	$(\text{F}+\text{S})_{\text{NA}}$

After the passivation treatments, the samples were subjected to Photoluminescence (PL) characterization the effect of various surface passivation

methodologies on electrical properties of GaAs surface. For PL study linearly polarized light produced by Argon Ion Power source, Spectra physics 165-Ar Ion Laser was used. Ar ion laser was fixed to operate at 150 mW (at source end). The light of excitation wavelength 530.15 nm, was focused on 10 μ m spot size. Fluorescence from the sample was detected by Photo multiplier tube (PMT).

3.2.4 Experimental procedure for electrochemical surface passivation:

Electrochemical passivation was performed utilizing potentiostate. The



samples were passivated in Flat cell unit as shown in Fig. 3.2.4.1. This cell ensured that only 1 cm² area of conducting GaAs face was exposed with electrolyte after being sandwiched between vertical cell wall and pressing metallic block. Pressing block is directly connected to power supply. In order to establish the electrical connection between front GaAs face and metallic block, indium (99.999%) was deposited on either side of GaAs and then both side were connected by spreading indium metal from front to back at few places. On the front side, indium was deposited through thermal evaporation at 10⁻⁶ torr while in the backside indium was spread using a soldering rod. The cross connection between front and back were also established using soldering rode Fig 3.2.4.2. Prior to electrochemical sulfide deposition, the GaAs samples were degreased and deoxidized following the method described earlier. An aluminium mask of suitable size was fixed on the conducting side (front) of GaAs using double sided tape so that circular window of more than 1 cm² area was maintained for the exposure of this face to expose

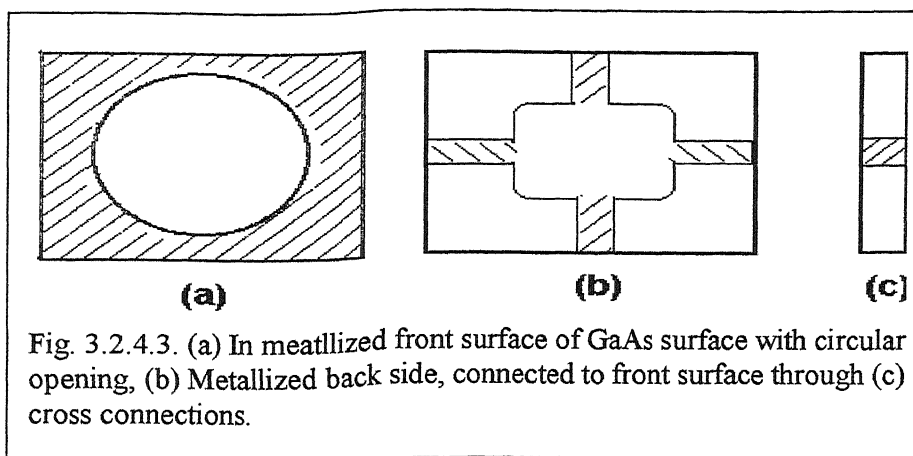


Fig. 3.2.4.3. (a) In metallized front surface of GaAs surface with circular opening, (b) Metallized back side, connected to front surface through (c) cross connections.

with electrolyte. After the metallization of the front side with aluminium mask, the tape was carefully removed from the sample surface and organic cleaning was carried out to remove organic contaminants. Indium metallization on backside of GaAs sample and

cross connection of the front and backside was then accomplished by soldering machine. Next metallized samples were annealed at 400°C for 6 min in hydrogen ambience to establish ohmic contact between indium and conducting face of GaAs. Metallized samples were placed in crucible and hanged in crucible furnace at 400 °C for 6 minutes with help of suitable platform and then H₂ was flown inside the furnace.

Two electrolytes, Na₂S salt solution in tert-butanol and NH₄F salt solution in deionized salt, were used in this part of study. The sample for electrochemical passivation was fixed in the working electrode position of the flat cell by careful tightening by the pressing metallic plate. The GaAs face was deoxidized by exposing to HCl:H₂O (1:4) solution at opening in the flat cell. In order to conduct deoxidation HCl:H₂O (1:4) solution was poured in cell and cell was tilted to bring GaAs surface and HCl solution in contact for a total of 2 min duration. The HCl solution was decanted from the cell and then DI water was poured inside the cell followed by shaking of the cell to rinse the sample thoroughly. After this step the electrolyte (Na₂S/t-C₄H₉OH or NH₄F/H₂O depending upon the aim) was poured in the cell and electrical contacts were established to the working electrode (GaAs sample), counter electrode (Platinum mesh) and reference electrode (silver/ silver chloride). A 263A, EG&G PAR Potentiostat was used to apply 1μA/cm² anodic current for 10 min. During anodic current charging potential of the

GaAs surface versus time was monitored. Finally, the sample was removed from the flat cell and the surface dried by blowing in dry nitrogen.

First electrochemical sulfide charging was first carried out using $\text{Na}_2\text{S}/\text{t-C}_4\text{H}_9\text{OH}$ electrolyte following the above-described methodology for passivation. In order to provide hybrid passivation treatment, the fluoride ion were electrochemically charged first from $\text{NH}_4\text{F}/\text{H}_2\text{O}$ solution and soon after completion of this step, the electrolyte was decanted and the cell was first washed with $\text{Na}_2\text{S}/\text{t-C}_4\text{H}_9\text{OH}$. The cell was then filled with the same sulfide solution the electrical connections were reestablished, and a $1\mu\text{A}/\text{cm}^2$ anodic-current density was applied for 10 min. At the end of the treatment, the sample was taken out of the cell and blown dried in dry nitrogen. These samples were then subjected to PL study.

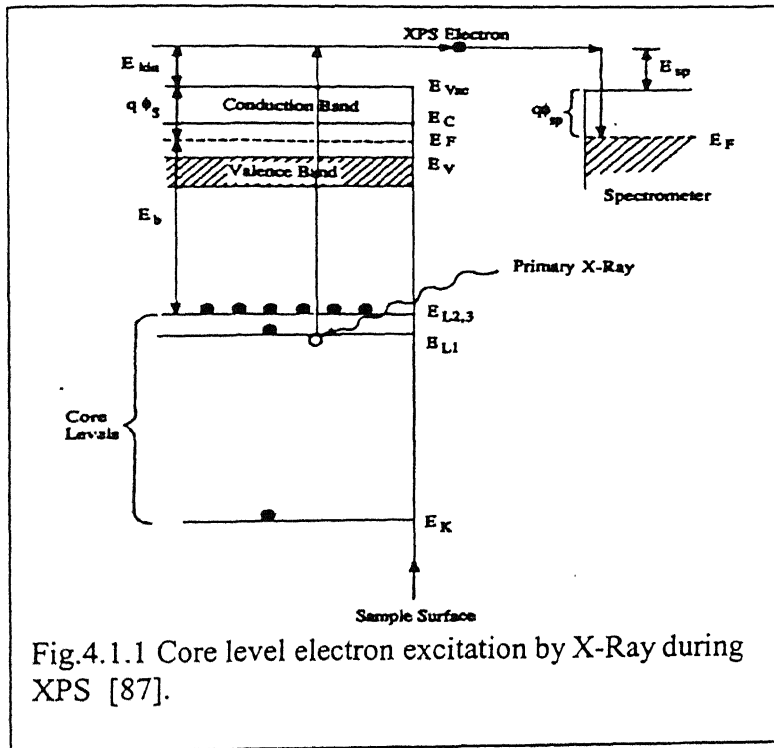
Chapter 4

Characterization methods

Effectiveness of surface passivation is evaluated by several characterization methods, which can provide details of change in surface chemistry and electrical properties. Over a period of time X-ray photoelectron spectroscopy (XPS) and Auger Electron Spectroscopy (AES) have been found very useful for investigating surface chemistry before and after passivation. The electrical properties of the passivated and unpassivated surface are evaluated with photoluminescence (PL) spectroscopy, Raman backscattering studies and current voltage method. The PL spectroscopy is very advantageous as no sample preparation is required for this study and qualitative analysis of passivated surface can be done immediately without further calculations. Following is the brief introduction of the important surface sensitive characterization methods used.

4.1 XPS: X-ray photoelectron spectroscopy (XPS) is one of the most extensively used methods to characterize the composition of GaAs surface after passivation. XPS is extensively used in semiconductor industry for solving variety of problems. XPS is very handy tool for determining the adhesion of film with material surface and inter-diffusion of interacting element in substrate layer. More importantly XPS is a surface sensitive method and emits photoelectron within 5-50 Å range. It provides the precise information of evolution and disappearance of bonds between surface atoms and interacting elements due to which XPS has become one of the most widely used method to characterize passivated surface.

XPS method is high-energy version of photoelectric effect. When X-ray beam with energy exceeding binding energy, impinge on sample surface, electron is emitted from core level upon X-ray energy. In this method, primary X-ray with high energy ejects photoelectron from the sample.



The photon-emitted electron will interact with spectrometer, a metal surface with Φ_{sp} work function, and will emit one electron with E_{sp} kinetic energy. The utilisation of E_{sp} along with work function of spectrometer and impinging primary X-ray energy provides the value binding energy (E_b) Fig.4.1.1.

$$E_b = h\gamma - E_{sp} - q\Phi_{sp}$$

The binding energy of electron depend upon its chemical surrounding due to which apart from revealing elemental state E_b also produces the chemical states. The availability of database of XPS results and graphs of binding energies for elements and compound provide strong support for the detection of elements and bonding nature during XPS study.

Example application of XPS in the field of surface passivation →

Results of XPS studies on sulfide passivated GaAs were presented by Sandroff et al. [37]. The XPS data were collected with a Kratos XSAM 800 photoelectron spectrometer equipped with a multichannel analyzer. Monochromatized Al K α X-ray was used as excitation source providing a resolution of 0.8eV for the Ag (3d $_{5/2}$) line. The core

level binding energy of As and Ga were referenced to the Ag(3d_{5/2}) line at 368.2 eV with an accuracy of 0.1 eV.

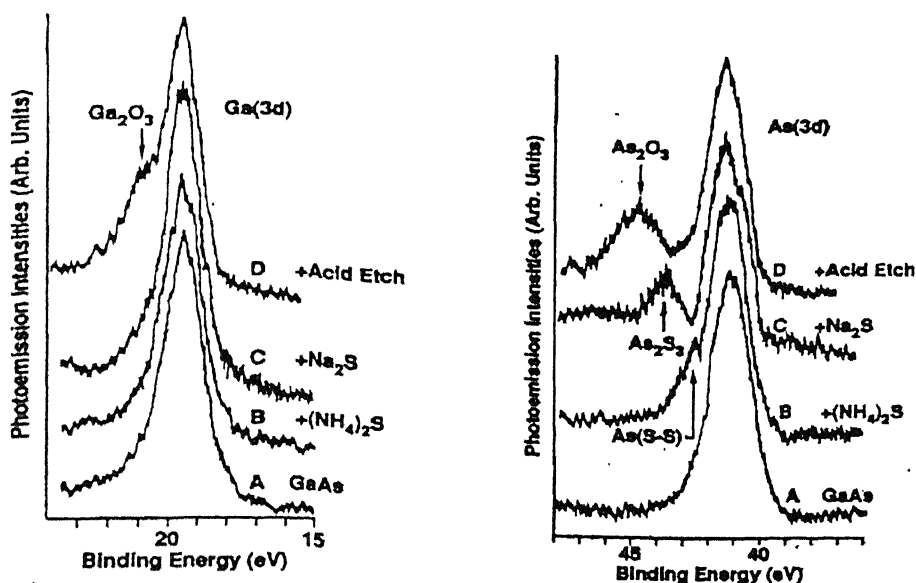
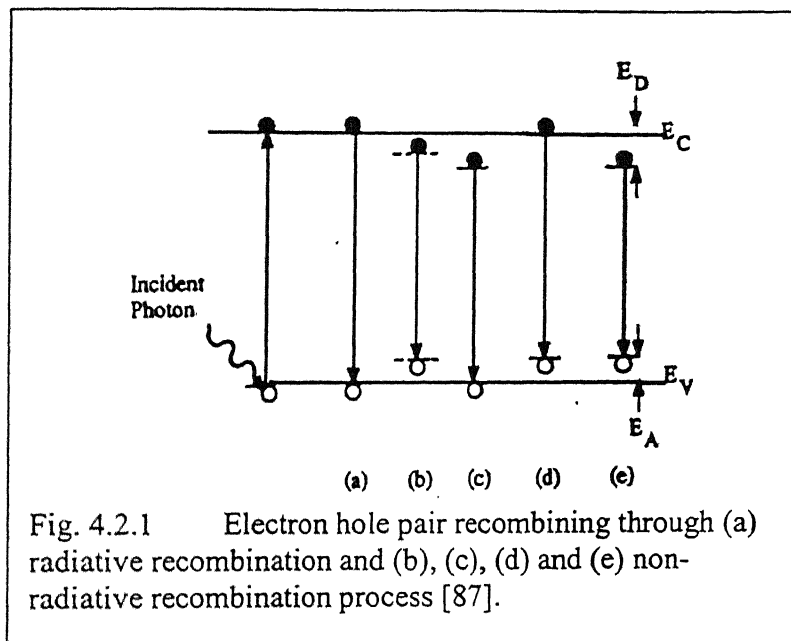


Fig.4.1.2 Ga(3d) and As(3d) core level spectra after various surface treatments of GaAs A clean surface, B treated with (NH₄)₂S, C treated with Na₂S.9H₂O and D acid etched surface [37].

Fig.4.1.2 exhibited the typical Ga(3d) and As(3d) XPS core level spectra of passivated GaAs(100) surface by Na₂S.9H₂O and (NH₄)₂S and compared with the cleaned and acid-etched GaAs. For acid etched surface peaks were shifted for higher binding energies with respect to the Ga (3d) and As (3d) core levels from GaAs. The peaks at 21.0 and 45.0 eV belonged to Ga₂O₃ and As₂O₃ respectively. Both the figures show that Na₂S.9H₂O and (NH₄)₂S solution passivation effectively removed the native oxide from the surface. In Ga (3d) XPS spectra no new peak or shoulder was observed following passivation treatment which implies that surface Ga atoms were not able to make observable amount of Ga-S bonds or a Ga_xS_y phase. The As (3d) XPS results are observed with a new peak Na₂S.9H₂O treated surface and a shoulder for (NH₄)₂S treated surface of GaAs. From this discussion it is clear that XPS is one of the most suitable method for determining the changes in surface chemistry of GaAs surface at various stage of passivation treatment.

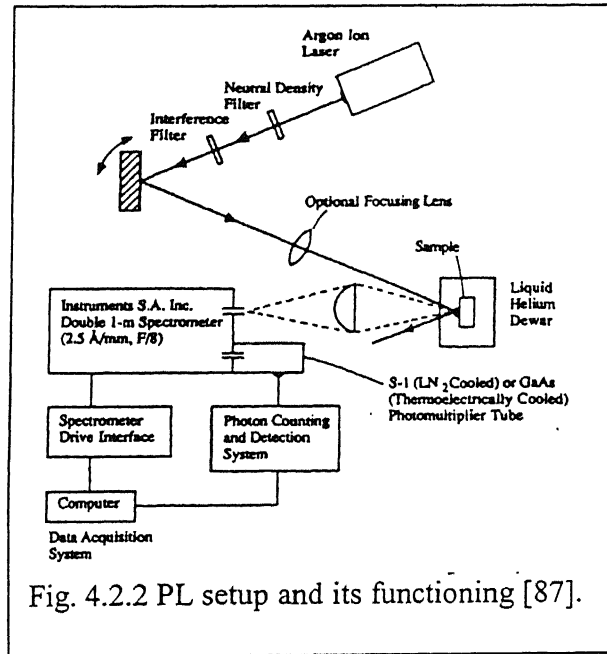
4.2 Photoluminescence (PL): PL is a non-destructive technique for the determination of shallow and deep level impurities and defects. The condition for PL measurement is that the radiative recombination should dominate non-radiative recombination. PL has been extensively used for evaluating the surface recombination velocity (SRV), which directly depends upon the surface state density. High surface state density increases the surface recombination velocity, which in turn reduces the event of radiative recombination [87].

Band gap is filled with surface states of both acceptor and donor nature. The



electrons and holes, which generate during laser beam exposure, generally recombine by travelling across the energy gap and emit radiation. However in the presence of surface states induced electronic levels first electron relaxes at their position then it recombines with the hole present in valance band. Due to which, event of photon generation during direct recombination have reduced due to the events of indirect recombination prompted by the presence of surface states Fig.4.2.1. The lesser is the number of radiadtive recombination smaller will be the PL intensity. Relative position of PL responses corresponding to semiconductor surfaces after various treatments, will directly exhibit the relative surface state density associated with them [38].

In principle, an optical source, invariably a laser with $h\nu > E_g$, is used. The laser beam gives genesis to electron hole pairs (ehp's) that recombine by one of several ways. Only for radiative recombination, photon is emitted, which is detected by suitable photon detecting unit. The PL signal intensity is directly proportional to the number of photons produced after radiative recombination. The reduction in surface state density by passivation of surface state produces change in PL response.

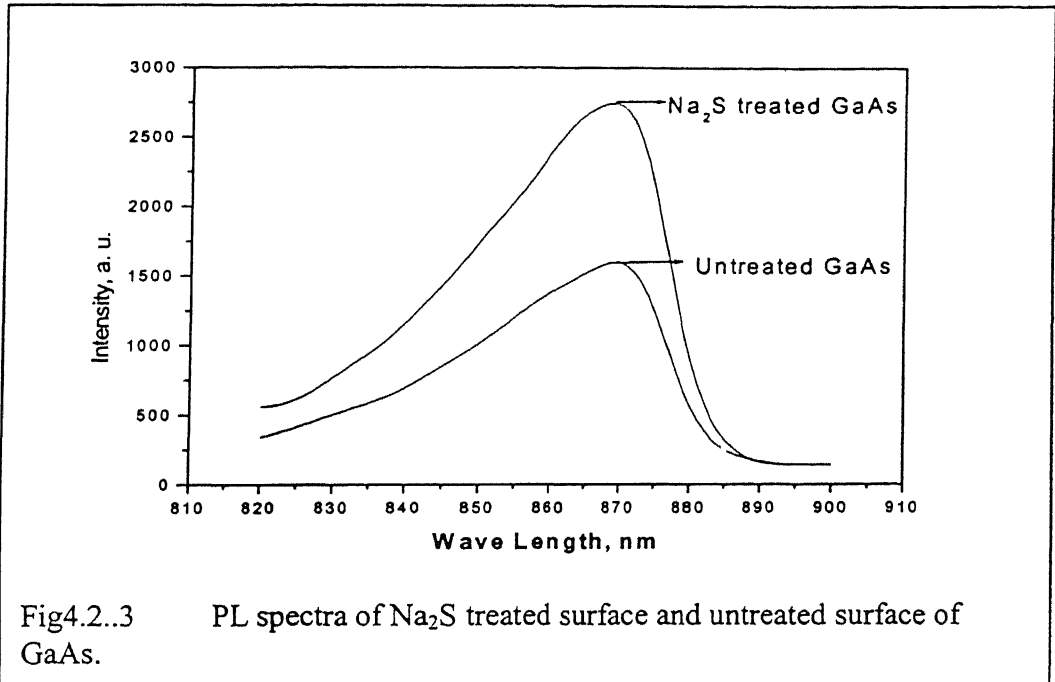


Typical representation of PL set up is shown in Fig 4. In the presence of surface states, event of radiative recombination reduces drastically.

Example application of PL study in the field of surface passivation → In present project photoluminescence study was conducted to characterize the efficacy of various passivation treatments. Typical PL spectra for a Na_2S passivated GaAs is presented in Fig. 4.2.2. The reduction in surface state density produced by the sulfide treatment of GaAs surface enhanced the event of radiative recombination, which directly affected the PLI intensity. Therefore PL response obtained from passivated GaAs surface is direct measure of extent of surface passivation.

The shape of PL spectra and the maximum PLI at approximately 870 nm was observed in all our studies which is in close agreement with the findings presented elsewhere on the same issue [10]. The fundamental reason behind the occurrence of maximum PL response at ~870 nm and PL spectra shape lies in the principle of

semiconductor device physics. There existed a number of school of thoughts apropos of basic reason behind PLI increase following surface passivation treatment. Extensive research work carried out on this subjects, as discussed in chapter 2, confirmed that the major reason behind PLI enhancement was quenching of surface state spectrum in energy band gap. The brief illustration of fundamental reason behind the shape of PL response and



the peak at ~870 nm in every spectra is following.

Before laser irradiation of GaAs surface the valance band is completely filled with electrons while the conduction band is completely empty. Shining light with energy higher than the band gap energy excites the electrones from valance band to conduction band leaving behind the empty slots (holes) in the energy levels near top of the valance band. In this stage the electron density in conduction band and holes density in valance band are represented by E_{FC} and E_{FV} quasi Fermi levels respectively Fig.6. This stage is called as complete inversion stage. Following this excitation the electrons in the conduction band relax to the bottom of the band by emitting phonons within 10^{-12} seconds. The relaxation time for the electron hole recombination (across the gap) is of the ordr of 10^{-9} seconds. It suggests that time required for climbing down to conduction band is neglible comapred to time required for the recombination process. As a matter of fact

above presented concept of recombination is oversimplified. It is well established that at finite temperature some of the states at the top of valance band are always occupied by electrons even in inversion state. It implies that all the electrones from the bottom of conduction band are not going to be recombined with the holes present in only one

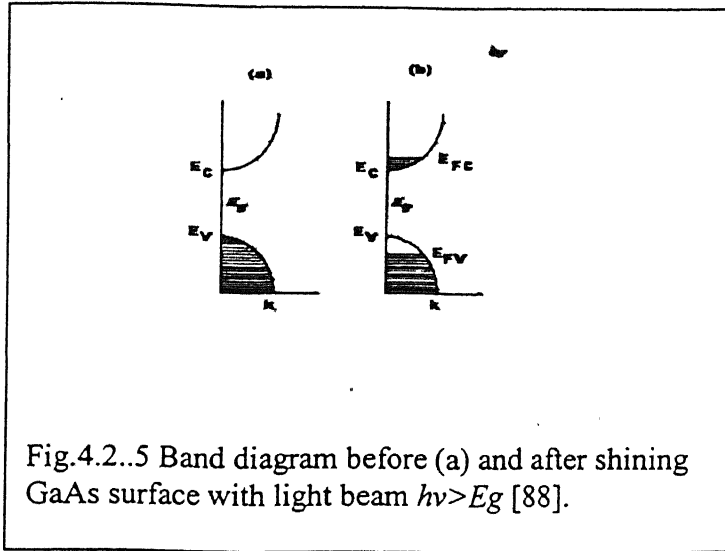


Fig.4.2..5 Band diagram before (a) and after shining GaAs surface with light beam $h\nu > E_g$ [88].

energy level. Excitation of valance band electrons with an light beam with $(h\nu > E_g)$ will produce electron and holes with E_C and E_V energy in conduction band and valance band. If the probability of finding an electron at energy E_C is $f(E_C)$ and finding the same electron at E_V is $f(E_V)$ for $h\nu > E_g$, the light output will be proportional to the $f(E_C) - f(E_V)$. Probability function follow the Boltzmann distribution due to which particular shape of the curve showing the light output intesity versus wavelength appears (inverted U shape, a charectistic of Boltzman distribution function.).

The energy of emitted radiation is given by

$$h\omega = E_g + E_C + E_V$$

$$\text{where, } E_C = \frac{h^2 k^2}{2m_e} \text{ and } E_V = \frac{h^2 k^2}{2m_h}$$

$$h = 1.05 \times 10^{-34} \text{ Js}$$

κ = wave vector
 m_e = effective mass of the electron
 m_h = effective mass of the hole
 ω = frequency of emitted radiation
 ν = frequency of the incident light beam

For that value of wave vector for which $f(E_C)-f(E_V)$ is maximum, the peak in the PL spectra will appear. In present case it was observed that peak of PL spectra was invariably present around 870nm. In present case for $k=0$ probability difference will be maximum which implies that emitted radiation intensity will be the highest at $h\omega=E_g$ [88].

Photoluminescence characterization is very useful for qualitative study of surface state density of GaAs requiring no specific sample preparation. It also consumes very less time for study once equipment is suitably calibrated. In this project all the surface passivation experiments are subjected to PL study for their evaluation.

4.3. Raman Spectroscopy:

Raman Spectroscopy is a vibrational spectroscopy method used for characterizing the change in surface properties of materials. It is primarily used for chemical analysis of surface. In the field of surface passivation of GaAs Raman scattering has been extensively employed to calculate surface barrier height after passivation treatment [40]. “When light is scattered from the surface of a sample, the scattered light is found to contain many wavelength that are incident on the sample (Rayleigh Scattering) but also different wavelengths at very low intensities (few parts per million) that represent an interaction with the material. The interaction of light with optical phonon is called Raman Scattering and the interaction of incident light with acoustic phonon results in Brillouin Scattering. Optical phonon have higher energies than acoustic phonons giving larger photon energy shifts. Hence Raman scattering is easier to detect than Brillouin scattering. Since the intensity of Raman scattered light is very weak, Raman spectroscopy is only practical when an intense monochromatic light source like a laser is available” [87]

Example application of Raman scattering study in the field of surface passivation →

The interaction of light with optical phonon has been used by several researchers to characterize the surface electrical properties of GaAs [36-38,40,51]. During one Raman study back scattering geometry configuration was so used in apparatus that

longitudinal phonon (LO) were observed [40]. The L^- and L^+ features were produced by scattering from the coupled phonons plasmons modes in the bulk where free carrier existed Fig. 7. The L^- component is more sensitive towards surface properties. For unpassivated sample, possessing high surface state density, value of L^- is below LO as free charges are conserved by surface states. For passivated surface, amount of free

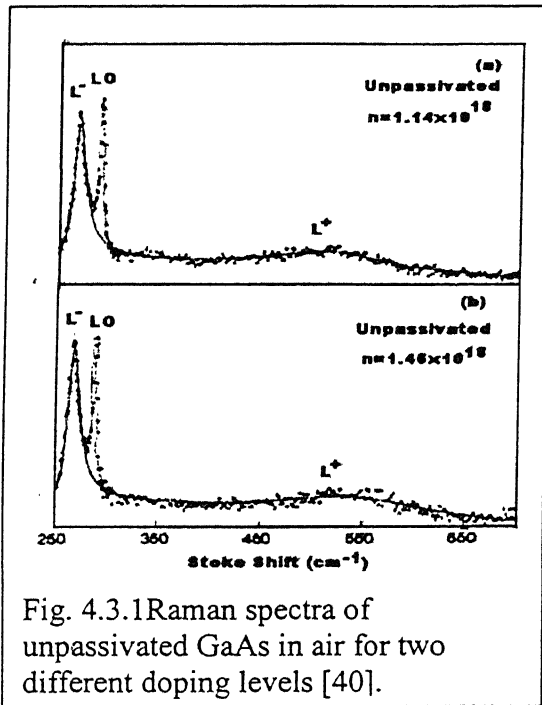


Fig. 4.3.1 Raman spectra of unpassivated GaAs in air for two different doping levels [40].

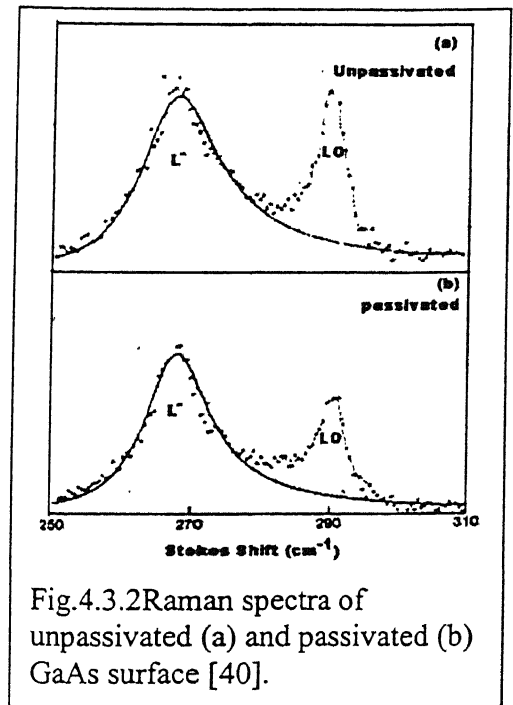


Fig.4.3.2 Raman spectra of unpassivated (a) and passivated (b) GaAs surface [40].

charge was not very much affected by surface states as surface states density reduced significantly by the passivation treatment. Due to which there existed significantly large value of L^- compared to LO.

For a doped opaque surface of semiconductor penetration depth D and depletion width δ , ($\delta < D$)

$$I(\text{LO}) = I_0(\text{LO}) (1 - e^{-2\delta/D})$$

$I_0(\text{LO})$ = LO phonon peak for undoped semiconductor

Similar relation is valid for phonon-plasmons peak.

$$I(L^-) = I_0(L^-) e^{-2\delta/D}$$

$I_0(L^-)$ = intensity of L^- peak (No depletion is present)

$$I(\text{LO}) / I(L^-) = I_0(\text{LO})(1 - e^{-2\delta/D}) / I_0(L^-) e^{-2\delta/D}$$

$I_0(\text{LO})/I_0(\text{L}^-)$ can be experimentally determined from the Raman spectra of unpassivated sample by equating $I(\text{LO})/I(\text{L}^-)$.

The value of surface barrier height V_s is calculated from

$$V_s = eN_D \delta^2 / 2\epsilon_0 \epsilon_s$$

The Raman method is found useful in calculating surface barrier height and depletion region near the surface without invoking intricate surface preparation.

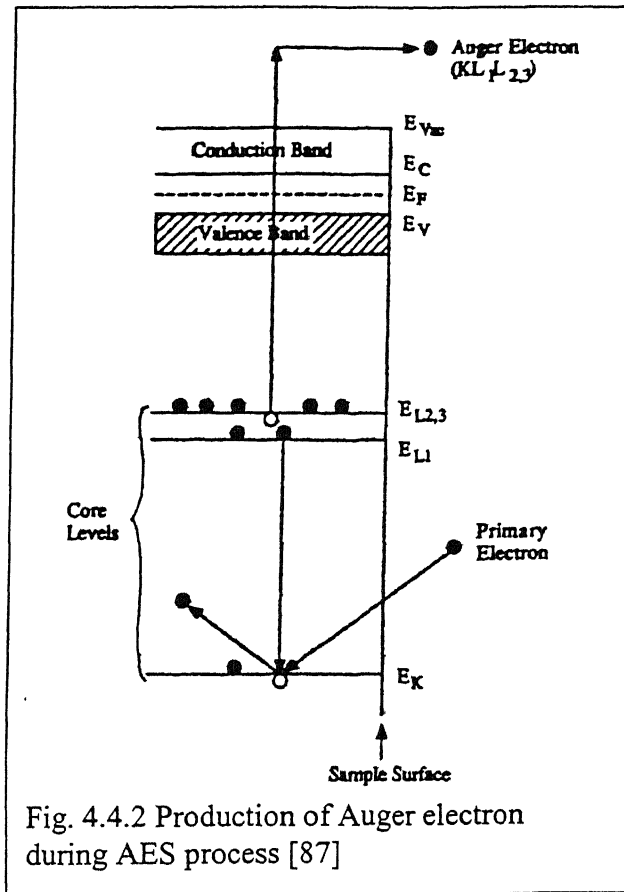
4.4 Auger Electron Spectroscopy (AES): AES is capable of detecting all elements except hydrogen and helium in the film. AES is very useful method for the study of chemical and compositional nature of materials. Data interpretation is significantly very easy if response from two elements that do not interfere. Moreover AES study is backed by large database with the advent of new developments in AES, information on chemical binding state has also become possible by decoding Auger transition energy shifts. AES can be used to study composition for thickness range from 5 to 50 Å. Following is the principle of AES.

Auger electron emission is presented in Fig.8 by the schematic diagram. Lets take an example of a semiconducting material having k level at E_k and two L levels at E_{L1} and $E_{L2,3}$. Primary electron from an energy source, excite an electron from the k shell to vacuum level. The K shell vacancy is filled by an electron from L_1 shell. Then energy $E = E_{L1} - E_k$ is adsorbed by third electron namely Auger electron belonging to $L_{2,3}$ level, which subsequently used for the chemical analysis purpose.

The complete process of Auger electron evolution is designated by K $L_1 L_{2,3}$ or KLL. However atoms remain in doubly ionised condition (that is why H and He can not be detected by AES). Following are the prominent Auger energy transitions directly dependent on atomic number Z Table4.4.1.

Table4.4.1: Range of atomic number and corresponding transition type.

Z	Transition type
$3 < Z < 14$	KLL
$14 < Z < 40$	LMM
$40 < Z < 82$	MNN



Auger electron forming deeper in the sample will lose energy to the extent of being undetectable in the background signal. The signal is readily noticeable when differential of $N(E)$ that is $dN(E)/dE$ is used.

Example application of AES in the field of surface passivation → Several researchers have employed AES for the determination of the presence of chemical elements on variously treated GaAs surface [63,76]. Ke et al. [76] used AES to exhibit the effect of annealing treatment on the chemical composition of GaAs surface Fig.4.4.3. From the spectra it is clear that carbon, oxygen and gallium has been significantly reduced whereas amount of sulfur remain unchanged.

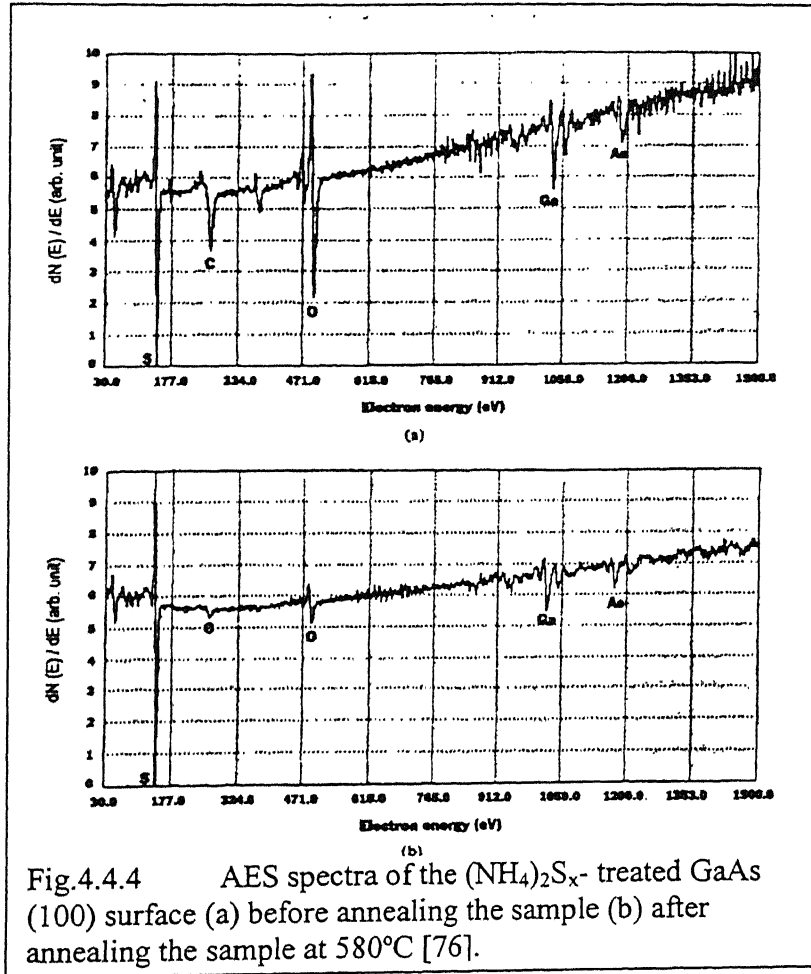
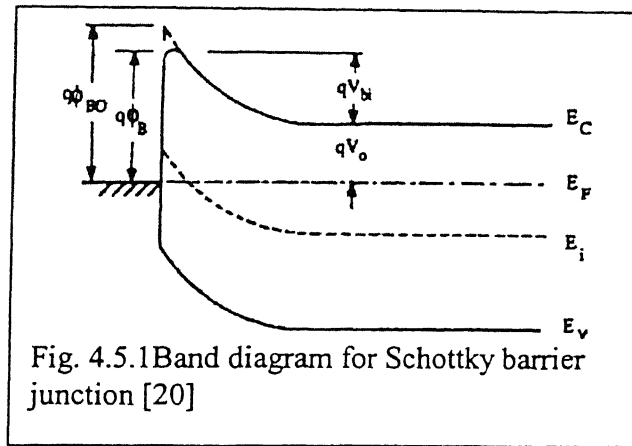


Fig.4.4.4 AES spectra of the $(\text{NH}_4)_2\text{S}_x$ - treated GaAs (100) surface (a) before annealing the sample (b) after annealing the sample at 580°C [76].

4.5 Current Voltage (I-V) measurement of Schottky Barrier (SB) Height: This is an electrical method used for the characterization of metal/semiconductor interface is discussed in this part. Schottky barrier diode, a representative electrical device present at metal/semiconductor (metal of suitable work function) is shown in Fig 4.5.1.

Φ_B is barrier height V_{bi} = built in potential and V_D is the potential of Fermi level with respect to the conduction band. The thermionic current voltage relation of SB diode is as follows

$$I = I_s(e^{qV/kT} - 1) \quad \text{-----} \quad (1)$$



Where I_s = saturation current = $AA^{**}T^2e^{-q\Phi_B/kT}$

$$I_s = I_{s1} e^{-q\Phi_B/kT}$$

A = diode area

$$A^{**} = A^* \times f$$

f = a factor depending upon optical

phonon scattering and quantum mechanical reflection.

$$A^* = 4\pi q k^2 m^*/h^3 = 120(m^*/m)A / \text{cm}^2\text{K}^2$$

Φ_B = effective barrier height

n = ideality factor

$$I = I_s e^{qV/nkT} (1 - e^{qV/kT}) \text{ is simplified version of (1)}$$

Generally barrier height is calculated from the current I_s . I_s is calculated by extrapolating $\log(I)$ versus V curve to $V = 0$. Point of intersection of extrapolated line on $\log(I)$ axis gives I_s . The barrier height is calculated from I_s by following.

$$\Phi_B = kT/q \ln(AA^{**}T^2/I_s)$$

However accuracy of this method is dependent upon knowledge of A^{**} . But being in ln term its effect may not be appreciable on calculation from two near temperature.

Example application of I-V method in the field of surface passivation → It has been observed by the number of researchers that sulfide passivation was effective in making metal/GaAs Schottky contacts sensitive towards metal workfunction. The current voltage measurement has been utilized for observing the change in surface barrier height following sulfide passivation. Carpenter et al. [13] used this electrical characterization to observe the surface passivation effect of sulfides on Schottky barrier height using exactly the above mentioned principle Fig. 4.5.2. Results of their I-V experiments manifested that

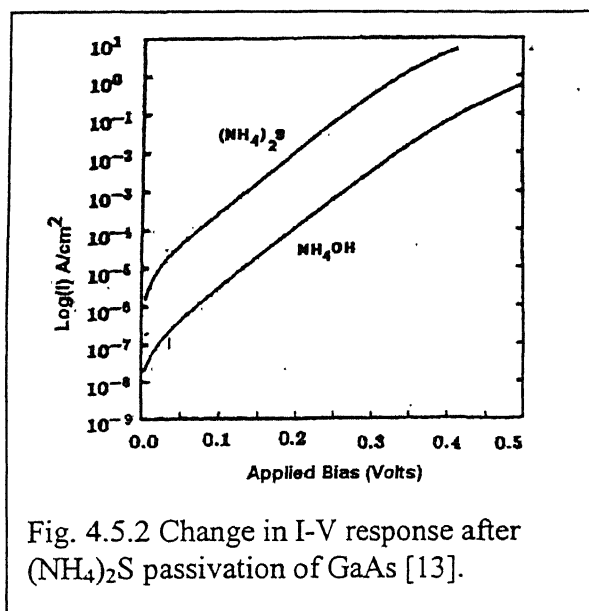


Fig. 4.5.2 Change in I-V response after $(\text{NH}_4)_2\text{S}$ passivation of GaAs [13].

sulfide passivation was affecting barrier height by unpinning the GaAs surface Fermi level. For instance schottky barrier height for gold increased from 0.781V to 0.841V. The shift in barrier height was attributed to the unpinning of Fermi level due the reduction in surface state density produced by sulfide treatment.

Chapter 5

Results and discussion

Passivation of n-doped semi-insulating GaAs surface was carried out using non-aqueous Na_2S /t-Butanol, non-aqueous NH_4F /t-Butanol and aqueous $\text{NH}_4\text{F}/\text{H}_2\text{O}$ solutions. During passivation either room temperature (RT) or 55°C was maintained. Mainly following two passivant charging methods, first by simple dipping of sample in fluoride/sulfide solution or electrochemical application of the passivants on GaAs surface, were employed. Both in dipping and electrochemical methods, either single or double step passivation scheme were used. For convenience in discussion, all the surface passivation scheme are designated with a particular name, exhibiting the passivant charged (see Table1).

Table1: Typical passivation conditions for particular surface passivation scheme and symbols assigned.

S. No.	Type of solution(s) containing passivant(s) in the order of their use, passivation temperature and passivant charging method.	Symbol
1	Na_2S /t-Butanol, RT, dipping sample in solution	S_{NA}
2	Na_2S /t-Butanol, $T=55^\circ\text{C}$, dipping sample in solution	$S_{\text{NA}55}$
3	NH_4F /t- Butanol, $T=55^\circ\text{C}$, dipping sample in solution	F_{NA}
4	$\text{NH}_4\text{F}/\text{H}_2\text{O}$, RT, dipping sample in solution	F_{A}
5	Na_2S /t-Butanol, $T=55^\circ\text{C}$, dipping sample in solution in the presence of ultrasonic vibrations	US_{NA}
6	Na_2S /t- Butanol, RT, Electrochemical charging of passivant	ES_{NA}
7	NH_4F /t-Butanol followed by Na_2S /t-Butanol solution $T=55^\circ\text{C}$, sample dipping in solutions	$F_{\text{NA}}S_{\text{NA}}$
8	$\text{NH}_4\text{F}/\text{H}_2\text{O}$ followed by Na_2S /t-Butanol solution, RT, sample dipping in solutions	$F_{\text{A}}S_{\text{NA}}$
9	$\text{NH}_4\text{F}/\text{H}_2\text{O}$ followed by Na_2S /t-Butanol solution, RT, Electrochemical charging of both F and S from respective solution	$EF_{\text{A}}S_{\text{NA}}$
10	Na_2S /t-Butanol followed by NH_4F /t-Butanol solution $T=55^\circ\text{C}$, sample dipping in solutions	$S_{\text{NA}}F_{\text{NA}}$
11	$\text{Na}_2\text{S}/\text{H}_2\text{O}$ followed by NH_4F /t-Butanol solution RT, sample dipping in solutions	$S_{\text{NA}}F_{\text{A}}$
12	Passivation in single solution prepared by dissolving both Na_2S and NH_4F reagents in t- Butanol, $T=55^\circ\text{C}$, sample dipping in solution	$(\text{F}+\text{S})_{\text{NA}}$

PL characterization of GaAs surface, passivated under different schemes was carried out and results are presented below.

The photoluminescence intensity enhancement (PLI) enhancement produced by $\text{NH}_4\text{F/t-Butanol}$ and $\text{Na}_2\text{S/t-Butanol}$ solutions at 55°C , on GaAs surface are summarized in Fig.1. In Fig.1, we have compared PLI enhancement (which represent reduction in surface state density present on GaAs and also implies the reduction of surface recombination velocity) for various treatment against the untreated one. In general PL intensity peak was always observed at or near 870 nm, which correspond to the band gap of GaAs. In fig.1 mean value of PL response has been plotted whereas the range of PLI enhancement for various treatment is shown in inset. Inset figure shows that there was significant eclipsing of range of PLI enhancement caused by $\text{S}_{\text{NA}55}$ and $\text{F}_{\text{NA}}\text{S}_{\text{NA}}$ passivation whereas rest of the treatment were out of the range of these two treatments but possessed overlapping of the range of PLI increase produced by them. In present study we will only make a comparison among mean values of PLI increase produced by various passivation increase. Based on the results, the $\text{S}_{\text{NA}55}$ passivation produced the maximum PLI enhancement whereas double step $\text{S}_{\text{NA}}\text{F}_{\text{NA}}$ passivation yielded the least PLI increment. The decreasing order of PLI increase caused by all the passivation treatments at 55°C is the following:

$$\text{S}_{\text{NA}55} > \text{F}_{\text{NA}}\text{S}_{\text{NA}} > (\text{S}+\text{F})_{\text{NA}} > \text{F}_{\text{NA}} > \text{US}_{\text{NA}} > \text{S}_{\text{NA}}\text{F}_{\text{NA}}$$

In order to evaluate the impact of temperature, for comparison with the results presented in Fig.1, we also conducted passivation treatment at RT. In addition, since non-aqueous fluoride treatment did not give desirable PLI enhancement we used aqueous fluoride solution, which possessed very high fluoride ion concentration compared to non-aqueous fluoride solution. But this attempt also could not produce improvement in surface electrical properties following changed fluoride passivation. The PL response recorded on passivated GaAs surface using $\text{Na}_2\text{S/ t-Butanol}$ and $\text{NH}_4\text{F/H}_2\text{O}$ at room temperature (RT) are presented in Fig.2. Double step $\text{F}_{\text{A}}\text{S}_{\text{NA}}$ passivation produced the maximum PLI enhancement whereas single F_{A} passivation brought about the least PLI increment. Range of PLI enhancement produced by various treatments significantly overlapped but remained away from untreated PLI range. Following decreasing trend of

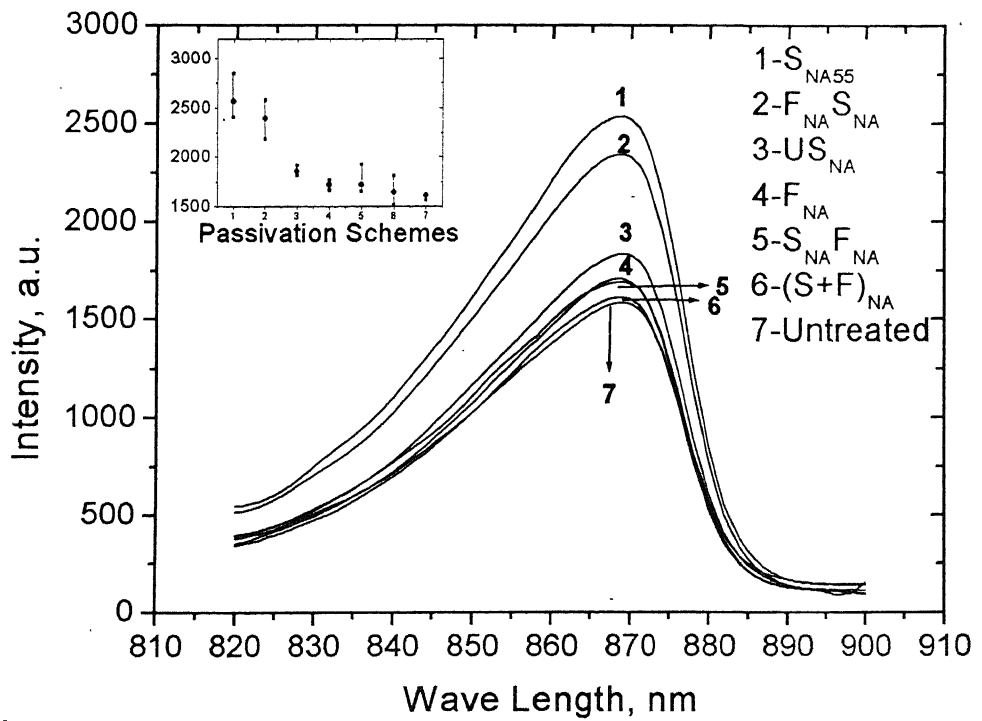


Fig.1 PL response from the GaAs surface passivated at 55 °C using non aqueous sulfide and fluoride solutions under different schemes.

PLI increase was observed after various passivation treatments of GaAs surface using above mentioned solutions and passivation temperature.

$$S_{NA} > F_A S_{NA} > S_{NA} F_A > F_A$$

We have also endeavored to study the effect of different passivant charging methods. For this purpose electrochemical passivant charging was carried out and its PL response was compared with GaAs surface passivated through simple passivant charging. (Dipping of GaAs sample in solution). The values of PLI enhancement caused by various passivation schemes utilized in this case are reported in Fig.3. The ES_{NA} passivation yielded higher increment in PLI compared to double step $EF_A S_{NA}$ passivation. The range of PLI increase produced by these two-passivation methods eclipsed. Moreover overlapping of range of PLI enhancement produced by $EF_A S_{NA}$ also overlapped with the small PLI increase range observed on untreated GaAs sample.

In order to acquire the quantitative information about the PL responses obtained from the GaAs surface passivated under different schemes, normalization of PL results was carried out. The PLI observed on unpassivated GaAs surface was assigned unit value and the PLI value for rest of the passivation schemes is calculated according to following formula and tabulated in Table2:

$$PLI = \frac{\text{PL peak for passivated sample}}{\text{PL peak for bare deoxidized sample}}$$

Table2: Increase in PLI produced by different surface passivation with respect to unpassivated GaAs surface.

S. No.	Type of passivation schemes used	PLI value for passivation at RT	PLI value for passivation at 55°C
1	Untreated GaAs surface	1.00	1.00
2	Sulfide Passivation	1.60 (S_{NA})	1.59 (S_{NA55})
3	ES_{NA}	1.65	-
4	US_{NA}	-	1.06
5	F_{NA}	-	1.07
6	F_A	1.09	-
7	$F_{NA} S_{NA}$	-	1.47
8	$F_A S_{NA}$	1.34	-

9	$EF_A S_{NA}$	1.18	-
10	$S_{NA} F_{NA}$	-	1.00
11	$S_{NA} F_A$	1.40	-
12	$(S+F)_{NA}$	-	1.15

Discussion: All the surface passivation schemes studied can be classified in two broad categories, first single step surface passivation and second double-step surface passivation of GaAs. In present section, the mentioned PL results are discussed in the light of published results and insights obtained during present work.

5.1 Single step passivation of GaAs surface→ In all, six single step surface passivation schemes were employed for GaAs surface passivation. Then these passivated samples were subjected to PL characterization and results are presented in Fig. 4 and Table 2.

These results clearly revealed that all the single-step S passivation except US_{NA} produced significantly higher PLI enhancement compared to PLI enhancement caused by single step fluoride passivation.

5.1.1 Effect of reagents on surface passivation→ Two reagents, Na_2S (source of sulfide ion) and NH_4F (source of fluoride ions) were utilized for the surface passivation of GaAs surface. The Na_2S reagent was incorporated in S_{NA} , S_{NA55} , US_{NA} and ES_{NA} passivation schemes whereas NH_4F reagent was utilized for F_A and F_{NA} passivation of GaAs surface. The effect of reagents on the surface chemistry and surface electrical properties of GaAs is discussed by considering representative S_{NA} passivation (for Na_2S reagent) and F_A passivation (for NH_4F passivation) in following paragraphs.

Bessolov et al.[49] have shown by XPS measurement that the peak intensity associated with Ga and As oxides decrease upon treatment with non aqueous Na_2S (dissolved in t-Butanol) solution and elemental As (As^0) peak remain intact while strong peaks of S bonded to As and Ga appeared. In other word S_{NA} and S_{NA55} helps in removing the oxide without affecting elemental As. The interaction of sulfur with GaAs surface produced the improvement in surface barrier height and reduction in surface recombination velocity and charge depletion region near surface [38]. In present case GaAs surface was deoxidized by HCl solution just before passivation which produced an

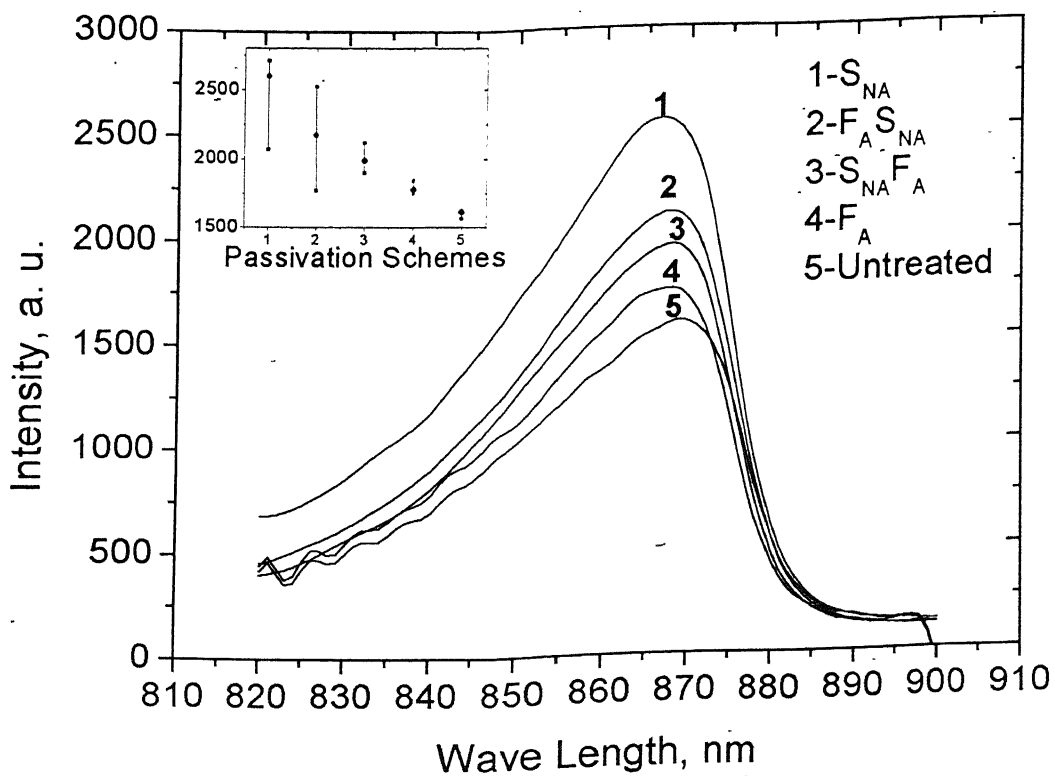


Fig. 2. PL response from the GaAs surface passivated at RT with non-aqueous aqueous fluoride solutions to study the effect of change in fluoride ion concentration on surface passivation.

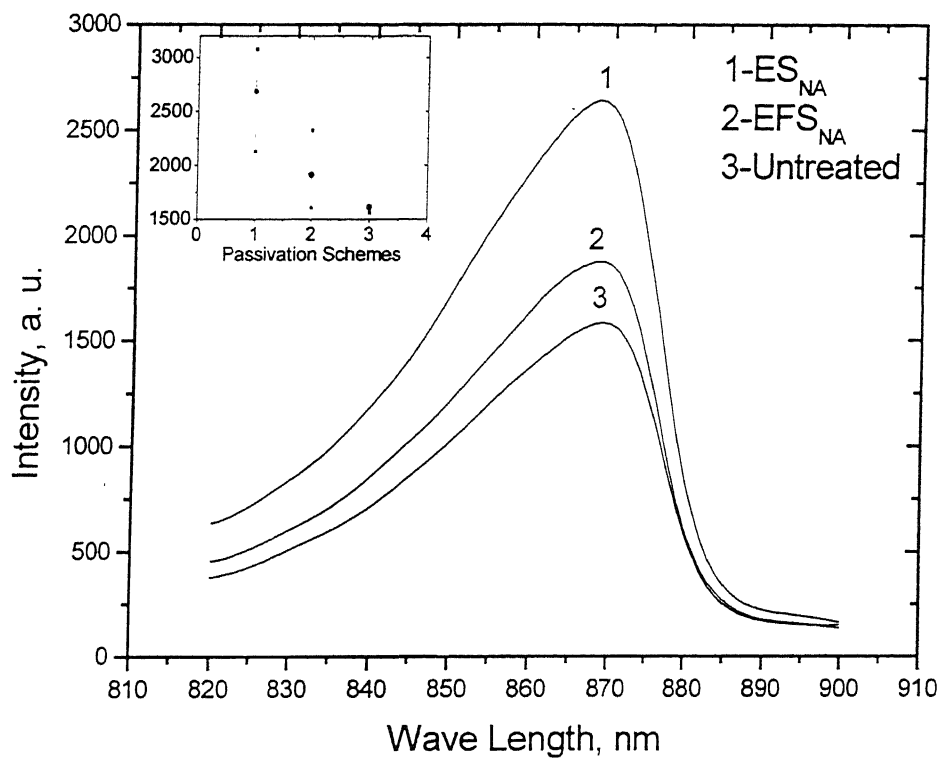


Fig.3. PL response from the GaAs surface passivated by electrochemical method for two superior passivation schemes according to earlier PL studies.

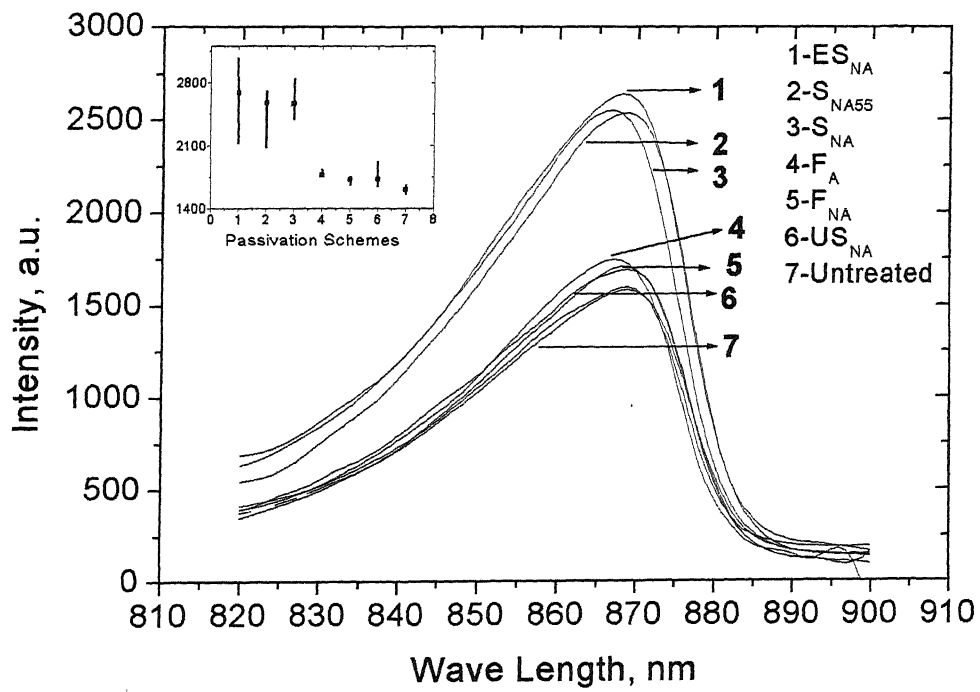


Fig.4. PL response from all single step passivated GaAs samples.

As rich GaAs surface [10]. We surmise that after sulfide passivation there will be higher number of As-S bonds compared to Ga-S bonds. According to theoretical calculations formation of As-S bonds gave genesis to new surface states in the band gap, whereas for Ga-S bond formation did not produce extra surface state [43,44]. It was experimentally shown that formation of Ga-S bond improved the surface electronic properties [75]. According to tight binding calculations efficacy of S_{NA} passivation was limited by the presence of As-S bonds [43].

From the published results it can be concluded that for effective surface passivation higher number of Ga-S bonds are desirable and an efficient passivation process should facilitate their formation. According to Bessolov et al. sulfur passivation was able to affect the overall spectrum of surface states on GaAs surface to improve surface electrical properties and it was shown that passivated GaAs surface possessed significant density of Ga-S bonds which was negligible in case of aqueous sodium sulfide passivation [51].

The F_A passivation (using NH_4F reagent) did not produce any passivation. In order to explain the results of F_A treatment it is important to consider the post passivation surface chemistry of GaAs. Table 3 contain the compounds of Ga and As with fluorine atoms. It appears that desorption of volatile arsenic fluoride leave GaAs defective due to which passivation of GaAs was not possible.

Table 3: compounds of Ga and As elements with fluorine and their enthalpy, melting point (M.P.) and boiling point (B.P) [89].

Compound	Enthalpy (kJ/Mole)	M.P. (°C)	B.P. (°C)
AsF ₃	146	-6.0	58/62
AsF ₅	484	-	-52.8
GaF ₃	-	1000	950
GaF ₃ .3H ₂ O	-	140	-

5.1.2 Effect of solvent dielectric constant /passivant concentration: Dielectric constant of solvent used in passivation study play a crucial role in improving surface electronic properties. Concentration of a passivant in a solvent is directly related to the solvent dielectric. Konenkova [52] have proposed following on the basis her experimental work. “The density of surface states pinning the Fermi level should decrease with the increase

of global hardness of electron cloud of atom or ion after sulfide passivation. It has been shown that the hardness of sulfur ion increase with the decrease of charge of ion and with the decrease of dielectric constant of the solvent. It has been found that treatment of GaAs (100) in alcoholic sulfide solution result in effective surface passivation. With the decrease of solution dielectric constant the sulfur surface coverage increases, the thickness of native oxides layer decreases and efficiency of band edge photoluminescence increases. These dependencies are stronger for solutions of strong base salt (e.g., sodium sulfide) than for that of weak base salt (e.g., ammonium sulfide)" [52]. In this project we studied the passivation effectiveness non-aqueous sodium sulfide solution (Na_2S dissolved in t-Butanol, a low dielectric constant solvent). We observed remarkable improvement in surface electronic properties, implied by the PLI enhancement compared to untreated sample after passivation treatment. It appears that during S_{NA} , S_{NA55} and E_{SNA} passivation significant reduction in surface state density have occurred, which gave rise to PL intensity enhancement.

We also studied the passivation capabilities of NH_4F salt dissolved in t-Butanol on GaAs surface at. 55°C . In our view, non-aqueous fluoride solution has not produced any passivation effect see Table 2. In order to explore the cause fluoride ion concentration in this solution was determined, which was found to be 0.75 mg/liter. Suspecting that fluoride ion concentration was very low in above mentioned alcoholic fluoride solution for passivation purpose aqueous solution of NH_4F , with 222000 mg/liter fluoride ion concentration, was utilized for the passivation of GaAs surface but this time at RT. In this case also we did not find noticeable improvement in surface electronic properties. We conclude that fluoride does not passivate GaAs surface, at least under the domain of our experimental conditions.

5.1.3 Effect of temperature on single step passivation: Temperature effect on the surface passivation was only studied for sulfide passivation. For this S_{NA} and S_{NA55} passivation were carried out RT and 55°C respectively, keeping all other parameters same. Results presented in Table 2 and Fig.4 shows that almost equal PLI enhancement was exhibited by sulfide passivation carried out at both the temperatures. This observation contradicted

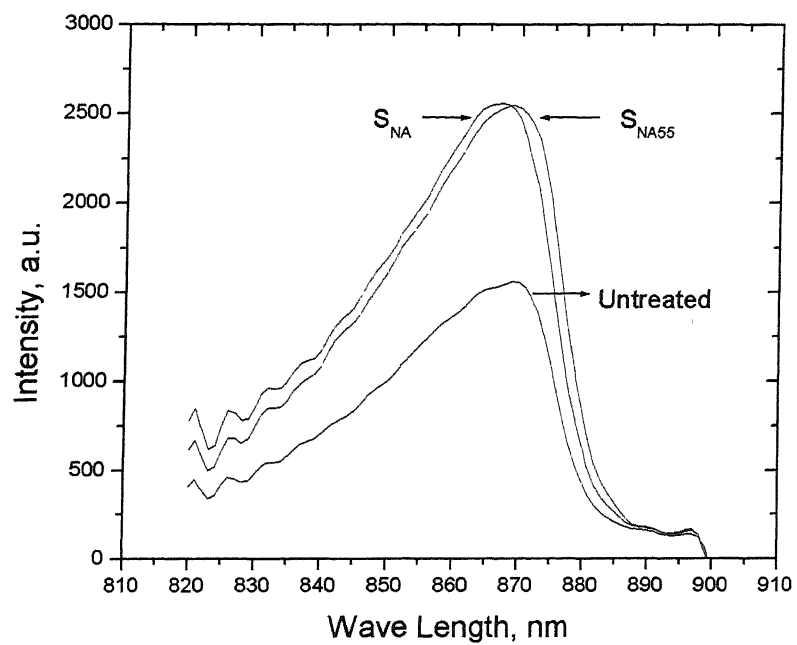


Fig. 5. Effect of temperature on sulfide passivation.

with the PL results presented in ref. [18], according to which PLI enhancement on sulfur passivated GaAs surface increased with the increasing temperature. It was shown that with the increasing temperature GaAs surface chemistry start changing from As rich ($\text{As/Ga} > 1$) to more stoichiometric ($\text{As/Ga} = 1$) surface composition [27]. In addition, increasing passivation temperature also provided activation energy to produce higher number of Ga-S bond, which exhibited better electrical properties compared to As-S bond [22]. In present work no improvement in PLI enhancement was detected with increasing passivation temperature. It may be due to the fact that the change in passivation temperature from RT ($\sim 30^\circ\text{C}$) to 55°C was too small to activate both the changes in surface chemistry and the formation of Ga-S bonds, which directly affects the surface recombination velocity and so the degree of PLI enhancement.

5.1.4 Effect of change in passivant charging method: Passivant charging method from dipping the sample in passivant containing solution to electrochemical charging was also attempted for sulfide passivation. Based on the average peak intensity of PL, presented in Table 2 and Fig. 4, slight improvement is obtained upon electrochemical treatment. The result of ES_{NA} passivation can be easily discussed under the light of previous studies made on electrochemical passivation using other type of electrolytes [55-57].

It is well established that electrochemical sulfide passivation produced Ga and As sulfides with higher oxidation number (O. No.) such as Ga_2S_3 (+3 O. No.) and As_2S_5 (+5 O. No.) along with GaS (+2 O No.) [56]. Sulfides with higher oxidation number have been observed to provide superior interface quality compared to low oxidation number

sulfides exhibiting improved electrical properties of GaAs surface and higher strength of sulfide ion bonding with GaAs surface [91].

The small magnitude increase in PLI ensuing ES_{NA} passivation compared to PLI enhancement yielded by S_{NA} passivation, do not commensurate with the result presented in ref. [55]. The reason may be inadequate supply of anodic current and less charging time. For comparison purpose value of anodic current and charging time used by several researchers are given in Table 4.

Table 4. Anodic current density and sulfide charging time mentioned in literature.

Anodic current density ($\mu\text{A}/\text{cm}^2$)	Charging time (minutes)	Reference
1	10	Present work
1-10	30	57
500	5	39
500	Few minutes	56
1000-10000	Few minutes	55

Above table clearly suggests the need of optimizing current density and charging time for exploiting the full potential of electrochemical charging. The XPS study of electrochemically passivated GaAs surface will also be helpful in understanding the surface passivation mechanism with the changed methodology.

5.1.5 Effect of ultrasonic vibration on single step passivation: The effect of ultrasonic vibration was only studied for the sulfide passivation carried out at 55°C (Designated as US_{NA}). Surface electronic properties akin to untreated GaAs surface were observed. Lunt et

al. [10] showed that sulfide passivation effect vanished by simple water rinsing. We surmise that presence of ultrasonic vibrations did not allow S to bond with GaAs surface.

5.2 Double step passivation:

We studied the passivation effect of sulfide and fluoride ions when applied on GaAs surface in conjunction with one another. $F_{NA}S_{NA}$, $S_{NA}F_A$ and F_AS_{NA} yielded the significant reduction in surface recombination velocity by reducing the surface state density, but the extent was lower than single step sulfide passivation treatments. Other double step passivation $S_{NA}F_{NA}$ and EF_AS_{NA} passivation produced nil and nominal PLI enhancement. It appears that application of fluoride ions before, after and along with sulfide ions for the passivation of GaAs surface deteriorated the effect of individual sulfide passivation. In those cases where fluoride solutions were used prior to sulfide passivation step, it seems formation of volatile arsenic fluoride, as shown in Table 3 created surface defects which enhanced the density of surface states density, to be passivated in second sulfide passivation step.

In case of $F_{NA}S_{NA}$ passivation non-aqueous fluoride solution was incorporated which possessed very small fluoride ion concentration (0.75 mg/liter), whereas in the F_AS_{NA} passivation aqueous fluoride solution (222000 mg/liter) was utilized. Which form the reasoning behind better $F_{NA}S_{NA}$ passivation. In former case surface defects are likely to be significantly less compared to F_AS_{NA} passivation because the presence of high fluoride ion concentration may enhance the event of volatile arsenic fluorides formation. Other likely reason behind the superior PL response produced by the $F_{NA}S_{NA}$ passivation, assuming that fluoride ion concentration in this case was sufficient to impart same effect

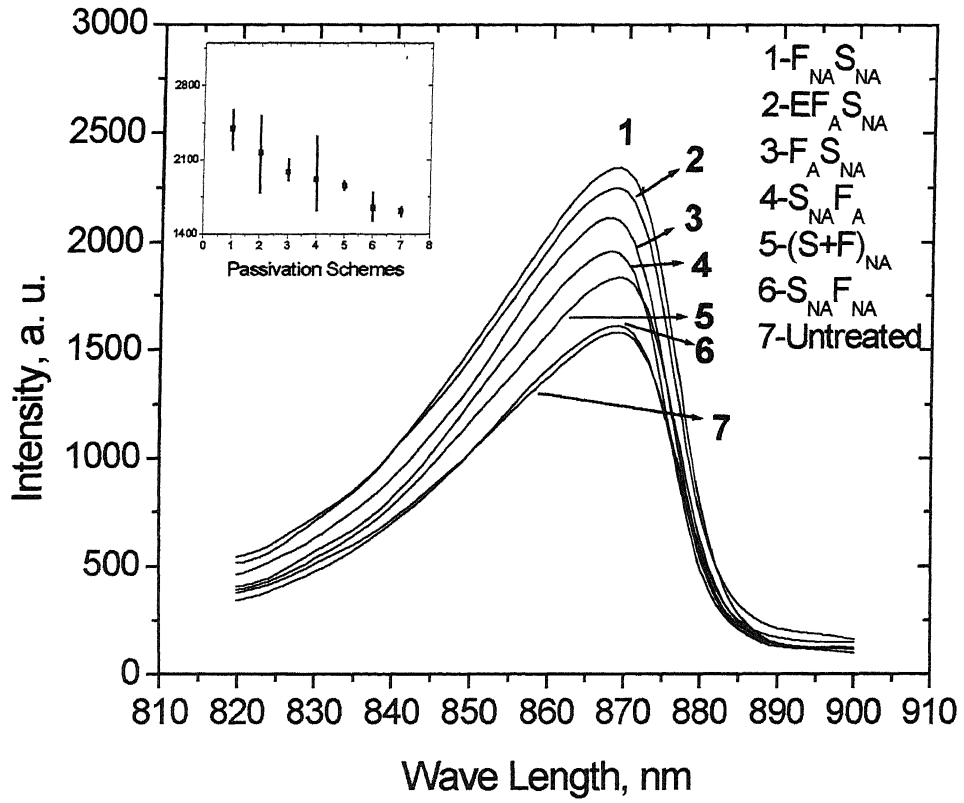


Fig. 6 PL response from all double step passivated GaAs samples.

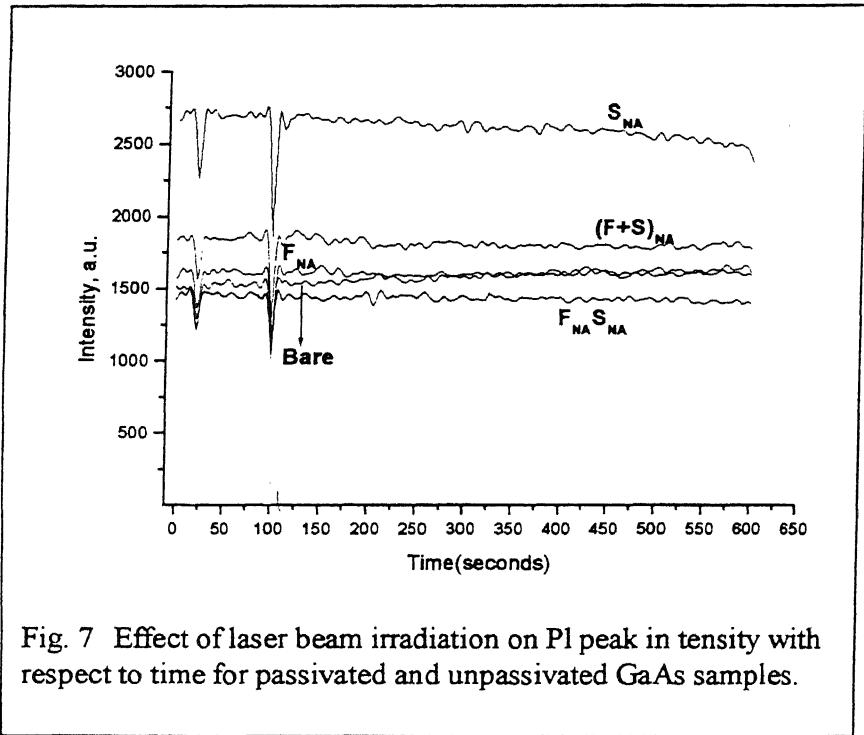
as occurred during $F_A S_{NA}$ passivation, can be explained in terms of passivation temperature. AsF_3 fluoride, with boiling point $58^\circ C$ is likely to desorb to a greater extent around $55^\circ C$ temperature during $F_{NA} S_{NA}$ passivation. It will prompt a relatively stable surface to be passivated during second step (sulfide passivation), carried out at RT, will result in a unstable GaAs surface, having a significant amount of volatile fluoride, which may be continuously desorbing from the surface even at room temperature. Passivation of this relatively unstable fluoride treated surface is likely to produce inferior surface electrical properties after the second sulfide passivation step.

$S_{NA} F_A$ and $S_{NA} F_{NA}$ schemes were executed to observe the effect of reversing the passivant charging order, $S_{NA} F_{NA}$ passivation did reproduce the untreated GaAs surface electrical properties, which indicates that effect of sulfide passivation in first step was completely vitiated by fluoride passivation. We may invoke the reasoning based on volatile compound formation here. According to which either some kind of non-passivating compounds or desorbs the significant part of sulfide by converting it into volatile compound prompting the depassivation of GaAs surface. In case of $S_{NA} F_{NA}$ it appears this reasoning fits appropriately. In $S_{NA} F_A$ passivation significant PLI enhancement was observed which hinted that probably the availability of high fluoride ion concentration at low passivation temperature produced some stable compounds that brought about observed surface passivation. However reaction kinetics may be altogether different in these two cases as two major determinants concentration and temperature are significantly different from one another.

For $(S+F)_{NA}$ passivation, in which both sulfide and fluoride passivants were charged together, PLI enhancement was also very less whose reason again is probably

$$F_{NA} > F_{NA}S_{NA} > (F+S)_{NA} > S_{NA}$$

It seems that wherever fluoride ions were utilized in passivation schemes, GaAs surface became more resistant towards laser irradiation and air exposure.



Conclusions

Passivation of GaAs surface attempted by utilizing sulfide and fluoride passivants individually and in different combinations. PL studies shows following results.

- (1) Single step sulfide passivation schemes yielded the highest reduction in surface recombination velocity. The change in passivant charging methodology from dipping of sample in sulfide solution to electrochemical sulfide charging did nominally improve the efficacy of single step sulfide passivation. Optimization of charging current and charging time can further improve the surface electrical properties and stability. Sulfide passivation carried out in the presence of ultrasonic waves did not produce its usual high degree deactivation of surface state density. Single step fluoride passivation did deactivate the surface state density to significant extent.
- (2) Out of double step passivation schemes $F_{NA}S_{NA}$, $S_{NA}F_A$ and F_AS_{NA} passivation schemes deactivated the GaAs surface to significant extent but it was less than degree of passivation produced by single step sulfide passivation schemes. Double passivation schemes like $S_{NA}F_{NA}$ and $EF_{NA}S_{NA}$ produced nil and extremely low passivation. We surmise that fluoride treatment step of double step passivation form volatile compounds which militates against sulfide passivation effectiveness in subsiding the active surface problem of GaAs surface. Formation of these un-passivating volatile compounds depends upon the sequence of passivant charging and temperature maintained especially during fluoride treatment step.

Suggestion for future work

- 1- Higher temperature ($< 60^{\circ}\text{C}$) should be used with fluoride passivation. It will desorb unstable fluorides producing relatively stable surface.
- 2- Use NH_4OH as the deoxidant, prior to passivation step as it producing near stoichiometric GaAs surface.
- 3- Use optimum combination of anodizing current and charging time for electrochemical passivation.
- 4- Use AFM and other characterization method to crate insight about passivation film morphology and surface chemistry.
- 5- During double step FASNA , if first step is kept simple but at 60°C or near about and second step is electrochemical charging of sulfur resultant is likely to be better than single step Sulfide passivation.

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